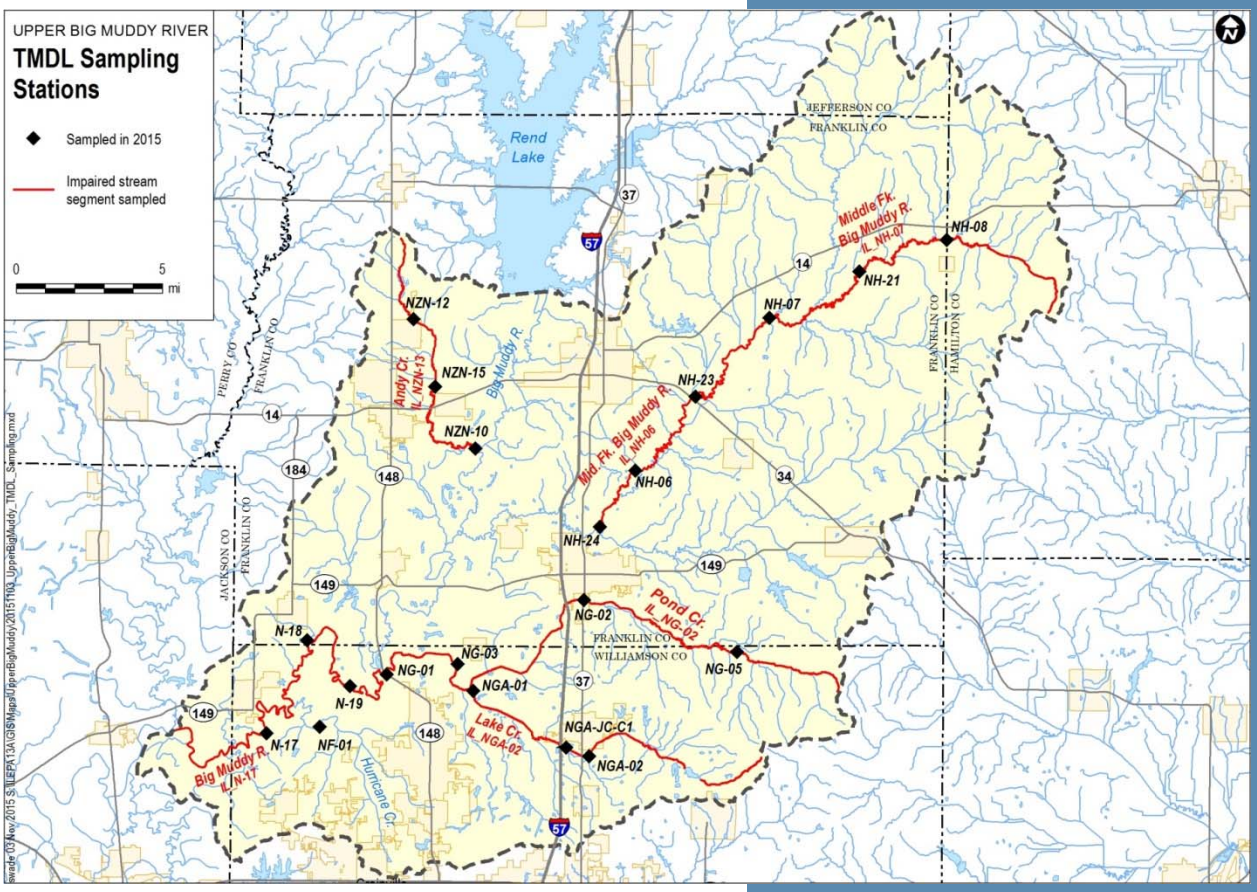

Stage 2 Report

for TMDL Sampling Activities in the Upper Big Muddy River Watershed, Illinois

Prepared for:
Illinois Environmental Protection Agency

March 2016

LimnoTech
Water Environment | Scientists Engineers

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1 Introduction

LimnoTech completed surface water sampling in September and October, 2015 to support Total Maximum Daily Load (TMDL) development for impaired waterbodies in the Upper Big Muddy River watershed. This report describes the field investigations and results of the sampling program. This report is divided into sections describing:

- Field investigation overview
- Water sample collection and field measurements
- Sediment oxygen demand and dissolved oxygen monitoring
- Quality assurance review

2 Field Investigation Overview

Monitoring was conducted within the Upper Big Muddy watershed in southern Illinois during summer 2015, in accordance with an Illinois EPA-approved Quality Assurance Project Plan (QAPP) (Attachment 1). Sampling was initially planned for summer/fall of 2014, but was delayed until 2015 due to wet conditions. Survey deployment in 2015 was based on real-time streamflow at United States Geological Survey (USGS) gages in and near the watershed.

The sampling and analysis activities included:

- collection of water samples for laboratory analysis;
- measurement of in-stream water quality and channel morphology parameters;
- stream discharge measurements;
- dissolved oxygen (DO) monitoring in the morning and afternoon; and
- sediment oxygen demand (SOD) measurements.

Water samples, stream and discharge measurements were collected from the selected locations during both events. SOD and morning/afternoon DO measurements were conducted at a subset of locations in each watershed.

Following the completion of field investigation and laboratory analysis activities, the generated data were compiled and a quality assurance review was conducted to assess data quality and usability.

Table 2-1 describes the sampling stations and presents field notes. One of the locations (NH-24) was inaccessible due to the presence of a locked access road gate with a no trespassing sign and was not sampled. Sampling locations are mapped in Figure 2-1.

Tables 2-2 and 2-3 present a summary of sampling conducted at each location during round 1 and round 2, respectively

Table 2-1. Sampling Locations in the Upper Big Muddy River Watershed

Stream	Access	TMDL Station ID	Notes regarding flow conditions and accessibility
Middle Fork Big Muddy	Deering Road/Co. Hwy. 5	NH-06	
Middle Fork Big Muddy	Illinois State Hwy. 34	NH-23	
Middle Fork Big Muddy	Unnamed lane west of Deering Road/Co. Hwy. 5 at W. Neal Rd	NH-24	Not accessible; locked access road gate/no trespassing sign
Middle Fork Big Muddy	Macedonia Road/Co. Hwy. 18/Co. Hwy 34	NH-08	
Middle Fork Big Muddy	N. Thompsonville Road/Co. Hwy. 17	NH-21	
Middle Fork Big Muddy	Bessie Road/Co. Hwy. 2	NH-07	
Andy Creek	Satch Road	NZN-15	
Andy Creek	Park Street Rd/Co. Hwy. 37	NZN-12	
Andy Creek	Forest cut/path north of Yellow Banks Road/Co. Hwy. 11 and west of Big Muddy River	NZN-10	
Big Muddy River	Cambria Road/Co. Hwy. 9	N-17	Higher than desirable flows
Big Muddy River	Pump Station Road/Lane	N-18	Higher than desirable flows; Not accessible during round 1 sampling.
Big Muddy River	Unnamed lane north of Clifford Road at Big Muddy Road	N-19	Higher than desirable flows
Hurricane Creek	N. Bend Road	NF-01	
Pond Creek	Illinois State Hwy. 148	NG-01	
Pond Creek	Freeman Spur Road	NG-03	
Pond Creek	Illinois State Hwy. 37	NG-02	
Pond Creek	Liberty School Road	NG-05	
Lake Creek	Stiritz Road	NGA-01	
Lake Creek	Binkley Road	NGA-02	
Lake Creek	Prosperity Road/Co. Hwy. 1	NGA-JC-C1	

Table 2-2. Round 1 Sampling Summary

Stream	Station ID	NH3, TKN, TP, oP, CBOD5, Chla, DO, water temp.	Flow (depth, velocity, channel morphometry)	SOD, DO (am and pm)
Middle Fork Big Muddy	NH-06	X	X	DO (am, pm) [no access for SOD measurement]
Middle Fork Big Muddy	NH-23	X	X	SOD, DO (2 am)
Middle Fork Big Muddy	NH-24	No access, locked gate/no trespassing sign		
Middle Fork Big Muddy	NH-08	X	X	
Middle Fork Big Muddy	NH-21	X	X	
Middle Fork Big Muddy	NH-07	X	X	SOD (alt. for NH-06)
Andy Creek	NZN-15	X	X	SOD, DO (am, pm)
Andy Creek	NZN-12	X	X	
Andy Creek	NZN-10	X	X	
Big Muddy River	N-17	X	No - Equipment failure	DO (am, pm) [no SOD-unsuitable substrate]
Big Muddy River	N-18	No access, locked gate/no trespassing sign		
Big Muddy River	N-19	X	No bridge access, unsafe to wade	SOD (alt. for N-17)
Hurricane Creek	NF-01	X	X	
Pond Creek	NG-01	X	X	
Pond Creek	NG-03	X	X	
Pond Creek	NG-02	X	X	SOD, DO (am, pm)
Pond Creek	NG-05	X	X	
Lake Creek	NGA-01	X	X	
Lake Creek	NGA-02	X	X	SOD, DO (am, pm)
Lake Creek	NGA-JC-C1	X	X	

Notes:

- NH3 (ammonia), TKN (Total Kjeldahl Nitrogen), TP (Total Phosphorus), op (ortho phosphorus), CBOD5 (5-day carbonaceous biochemical oxygen demand), Chla (chloropyll a), DO (Dissolved oxygen), SOD (sediment oxygen demand)
- Alternate locations were used for SOD as follows (NH-07 in place of NH-06; N-19 in place of N-17) for reasons described above.

Table 2-3. Round 2 Sampling Summary

Stream	Station ID	NH3, NO3, TKN, TP, oP, CBOD5, DO, water temp.	Flow (depth, velocity, channel morphometry)
Middle Fork Big Muddy	NH-06	X + Chla	X
Middle Fork Big Muddy	NH-23	X + Chla	X
Middle Fork Big Muddy	NH-24	No access, locked gate/no tresspassing sign	
Andy Creek	NZN-15	X	X
Andy Creek	NZN-12	X	X
Andy Creek	NZN-10	X	X
Big Muddy River	N-17	DO/water temp. only	X
Big Muddy River	N-18	X + Chla	
Big Muddy River	N-19	DO/water temp. only	

Notes:

- NH3 (ammonia), NO3 (nitrate), TKN (Total Kjeldahl Nitrogen), TP (Total Phosphorus), oP (ortho phosphorus), CBOD5 (5-day carbonaceous biochemical oxygen demand), Chla (chloropyll a), DO (Dissolved oxygen), SOD (sediment oxygen demand)

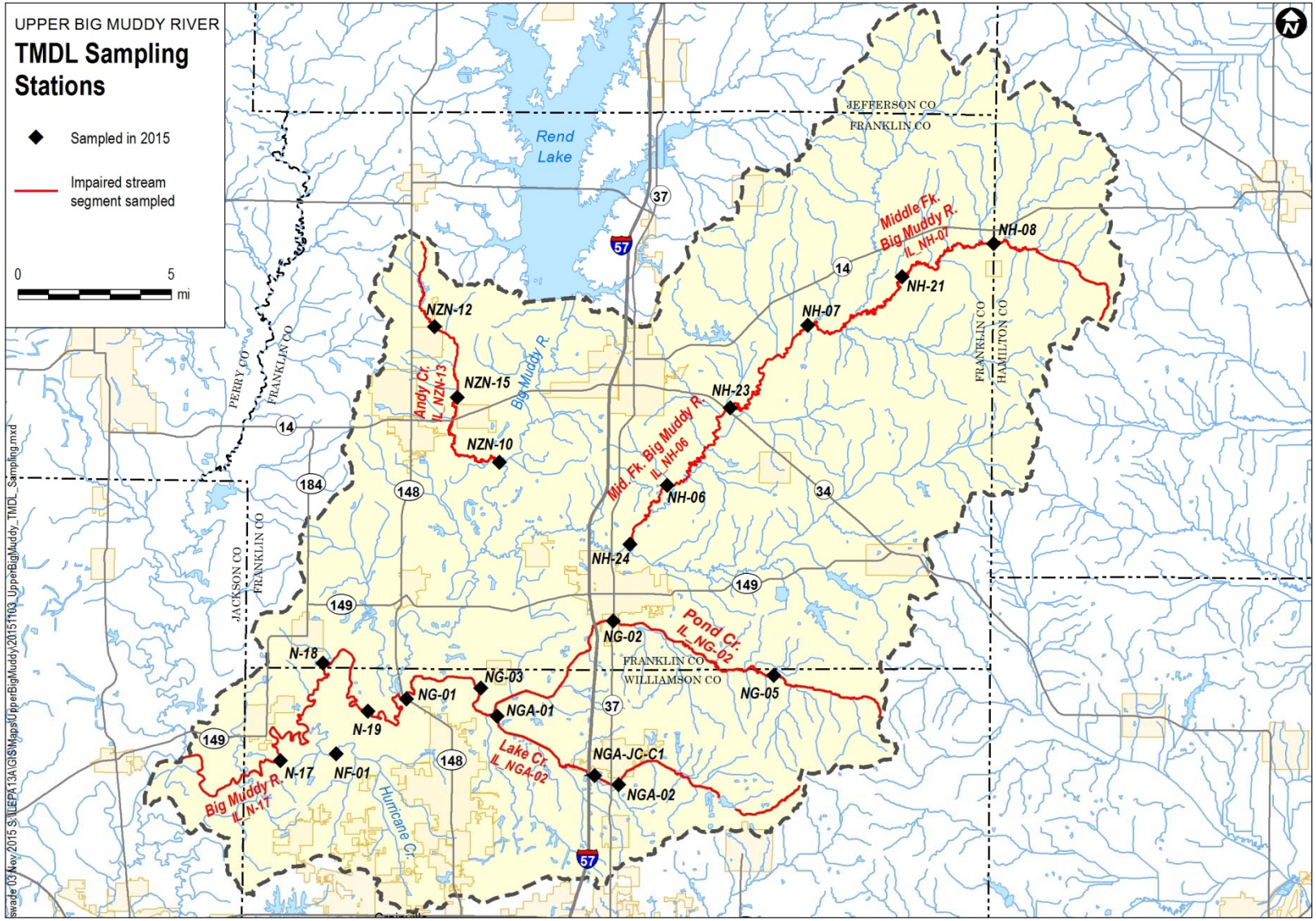

Figure 2-1 Upper Big Muddy River Watershed Sampling Locations

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3 Water Sample Collection and Field Measurements

Sampling activities were conducted in accordance with the QAPP during low flow conditions on two separate occasions (Round 1 and Round 2), with the exception of the Big Muddy River segment sampling locations which were at higher than median flows for both rounds of sampling. Stream segments impaired due to low dissolved oxygen were sampled twice if a permitted point source discharge was being considered as a potential source contributing to low dissolved oxygen. This assessment was based on an evaluation of point source discharge locations compared to IEPA sampling locations that the impairment assessments were based on. For example, if a stream segment is impaired due to low dissolved oxygen, but the impairment determination was based on data collected upstream of all point sources to that segment, then the stream was only sampled once.

Surface water samples and field measurements were collected at 19 stream locations (out of a possible 20 planned locations); Two locations (N-18, NH-24) were not sampled due to lack of access during the first round of sampling and one location (NH-24) was not sampled due to lack of access during the second round of sampling. The Big Muddy River was flowing above median levels for both sampling rounds, though at lower flows during the second round. All other stream locations were at low flows; generally flowing during the first round of sampling and generally not flowing during the second round of sampling. Water level conditions observed in the field are noted in Table 2-1.

Field instruments were used to measure in-situ water quality parameters, and TriMatrix Laboratories in Grand Rapids, Michigan, conducted all laboratory analyses except those for Chlorophyll a, which were conducted by the Great Lakes Environmental Center (GLEC) in Traverse City, Michigan under subcontract to TriMatrix. At all locations, water samples were collected for laboratory analysis of ammonia (NH3), total kjeldahl nitrogen (TKN), total phosphorus (TP), ortho phosphorus (oP), 5-day carbonaceous biochemical oxygen demand ($CBOD_5$) and chlorophyll a (Chla). During the second round of sampling, nitrate (NO3) analysis was added and Chla was only sampled at the Big Muddy and Middle Fork Big Muddy locations. Field measurements included dissolved oxygen (DO), water temperature (T), channel morphometry (water depth and width) and discharge measurements. Discharge was recorded using standard USGS techniques employing an electromagnetic point velocity meter (Marsh–McBirney Flo-Mate 2000) and a bridgeboard or a wading rod. Information supporting flow calculation was recorded in field notebooks and included:

- Site location,
- Date and time,
- Measurement monitoring point,
- Distance between measurement points,
- Depth at each measurement point,
- Velocities at each measurement point, and
- Any significant observations of monitoring procedures or river conditions.

Round 1 laboratory analytical and field measurement results are presented in Tables 3-1 and 3-2, respectively. Round 1 channel morphometry and discharge measurement results are presented in Table 3-3.

Round 2 laboratory analytical and field measurement results are presented in Tables 3-4 and 3-5, respectively. Round 2 channel morphometry and discharge measurement results are presented in Table 3-6.

Table 3-1. Round 1 Laboratory Analytical Results

Sample ID	Sample Collection Date Time	CBOD5 (mg/L)	Chla (mg/L)	NH3 (mg/L)	TKN (mg/L)	oP (mg/L)	TP (mg/L)
Middle Fork Big Muddy River							
NH-06	9/22/2015 13:20	8.9	0.04571	<0.050	1.1	0.03	0.122
NH-07	9/22/2015 11:20	<2.0	0.03011	<0.050	0.68	0.044	0.124
NH-08	9/22/2015 16:20	<2.0	0.01157	0.27	1.1	0.033	0.102
NH-21	9/22/2015 15:30	3.5	0.01669	<0.050	1.1	0.018	0.112
NH-23	9/22/2015 14:30	2.1	0.01375	<0.050	0.71	0.042	0.103
Big Muddy River							
N-17	9/23/2015 14:20	2.3	0.02903	0.068	0.73	0.111	0.252
N-19	9/23/2015 16:30	2.5	0.02954	0.069	0.94	0.128	0.228
Andy Creek							
NZN-10	9/23/2015 11:05	<2.0	0.00486	0.26	1.1	0.457	0.582
NZN-12	9/23/2015 10:15	<2.0	0.00467	0.061	0.63	0.047	0.0807
NZN-15	9/23/2015 9:30	<2.0	0.00352	0.47	1.2	0.214	0.245
DUP-1 (NZN-15)	9/23/2015 9:30	<2.0	0.0046	0.45	1.1	0.187	0.229
Hurricane Creek							
NF-01	9/23/2015 18:00	<2.0	0.00173	0.056	<0.50	0.125	0.161
Pond Creek							
NG-01	9/24/2015 11:30	<2.0	0.00166	0.06	0.66	0.109	0.174
NG-02	9/24/2015 9:20	5	0.03452	<0.050	0.84	<0.0100	0.132
DUP-2 (NG-02)	9/24/2015 9:20	5.4	0.03874	<0.050	1.1	<0.0100	0.132
NG-03	9/24/2015 10:00	<2.0	0.00806	0.051	0.66	0.091	0.135
NG-05	9/24/2015 16:40	2.6	0.02832	1.4	2	<0.0100	0.0565
Lake Creek							
NGA-01	9/24/2015 12:30	<2.0	0.02161	<0.050	0.53	0.133	0.151
NGA-02	9/24/2015 15:10	<2.0	0.00332	<0.050	<0.50	<0.0100	0.0218
NGA-JC-C1	9/24/2015 16:00	<2.0	0.00511	8.9	9.9	2.43	2.41
Field Blank Samples							
FB-1	9/22/2015 11:15	<2.0	<0.0003	0.2	<0.50	<0.0100	<0.0100
FB-2	9/24/2015 7:15	<2.0	<0.0003	<0.050	<0.50	<0.0100	<0.0200

Analyte Codes:
CBOD5 – Carbonaceous Biochemical Oxygen Demand
Chla – Chlorophyll a
NH3 – Ammonia Nitrogen
TKN – Total Kjeldahl Nitrogen
oP – ortho phosphorus
TP – Total Phosphorus

Table 3-2. Round 1 Field Measurement Results

Station	Collection Date Time	Dissolved Oxygen (mg/L)	Water Temperature (degC)
Middle Fork Big Muddy River			
NH-06	9/22/2015 12:18	12.03	19.72
NH-06	9/22/2015 18:15	13.32	20.36
NH-07	9/22/2015 10:11	6.06	19.1
NH-07	9/22/2015 10:16	6.31	19.1
NH-07	9/22/2015 11:20	6.86	19.64
NH-08	9/22/2015 16:20	3.04	19.11
NH-21	9/22/2015 15:30	4.87	21.18
NH-23	9/22/2015 14:30	7.91	19.31
NH-23	9/22/2015 17:53	9.75	21.6
Big Muddy River			
N-17	9/23/2015 7:32	7.43	21.19
N-17	9/23/2015 14:20	8.58	24.44
N-19	9/23/2015 16:47	8.36	22.6
N-19	9/23/2015 17:23	8.04	23.3
N-19	9/23/2015 17:30	8.05	23
Andy Creek			
NZN-10	9/23/2015 11:19	1.9	20.53
NZN-12	9/23/2015 10:15	4.47	17.6
NZN-15	9/23/2015 8:40	1.88	16.8
NZN-15	9/23/2015 8:49	1.6	16.7
NZN-15	9/23/2015 9:36	2.15	17.04
NZN-15	9/23/2015 12:20	1.94	18.5
Hurricane Creek			
NF-01	9/23/2015 18:01	7.84	20.97
Pond Creek			
NG-01	9/24/2015 11:30	9.12	19.47
NG-02	9/24/2015 8:44	7.54	17.7
NG-02	9/24/2015 8:45	7.35	17.7
NG-02	9/24/2015 9:27	7.08	17.65
NG-02	9/24/2015 14:19	14.77	25.97
NG-03	9/24/2015 10:03	6.52	19.01
NG-05	9/24/2015 16:47	15.33	20.65
Lake Creek			
NGA-01	9/24/2015 12:30	8.9	19.74
NGA-02	9/24/2015 7:52	7.01	17.14
NGA-02	9/24/2015 14:54	6.75	20.1
NGA-02	9/24/2015 15:00	7.49	21.3
NGA-02	9/24/2015 15:27	8.83	25.33
NGA-JC-C1	9/24/2015 16:03	3.5	20.76

Table 3-3. Round 1 Channel Morphometry and Flow

Station	Date	Stream Width (ft)	Average Water Depth (ft)	Average Velocity (ft/s)	Water Area (ft2)	Discharge (ft3/s)
Middle Fork Big Muddy River						
NH-08	9/22/2015 16:30	34	1.99	0.04	67.5	2.68
NH-21	9/22/2015 15:40	77	1.53	0.04	117.5	3.64
NH-07	9/22/2015 10:30	68	4.09	0.05	278.0	13.04
NH-23	9/22/2015 14:45	70	3.91	0.03	274.0	8.13
NH-06	9/22/2015 12:30	318	1.30	0.03	412.0	15.42
Andy Creek						
NZN-12	9/23/2015 10:20	20	0.24	0.00	4.8	0.01
NZN-15	9/23/2015 9:10	18	0.60	0.03	10.8	0.32
NZN-10	9/23/2015 11:10	14	0.43	0.03	6.0	0.21
Lake Creek						
NGA-02	9/24/2015 15:35	16	1.15	0.04	18.4	0.75
NGA-JC-C1	9/24/2015 16:00	17	1.04	0.03	17.6	0.68
NGA-01	9/24/2015 12:40	25	0.40	0.45	10.0	5.54
Pond Creek						
NG-05	9/24/2015 16:50	25	1.10	0.06	27.6	1.90
NG-02	9/24/2015 8:55	29	0.87	0.08	25.2	2.24
NG-03	9/24/2015 10:15	44	2.48	0.07	109.2	7.23
NG-01	9/24/2015 11:45	32	1.86	0.05	59.6	3.43
Hurricane Creek						
NF-01	9/23/2015 18:10	18	0.31	0.37	5.6	1.88
Big Muddy River						
N-17	9/23/2015 14:50	70	Not measured - equipment failure			

Table 3-4. Round 2 Laboratory Analytical Results

Sample ID	Sample Collection Date Time	CBOD5 (mg/L)	Chla (mg/L)	NO3 (mg/L)	NH3 (mg/L)	TKN (mg/L)	oP (mg/L)	TP (mg/L)
Andy Creek								
NZN-10	10/14/2015 13:15	<2.0	n/a	<0.050	0.39	1.1	0.449	0.479
NZN-12	10/14/2015 11:45	<2.0	n/a	<0.050	<0.050	0.51	0.115	0.154
DUP-3 (NZN-12)	10/14/2015 11:45	<2.0	n/a	<0.050	<0.050	0.52	0.114	0.162
NZN-15	10/14/2015 12:20	<2.0	n/a	0.065	1.7	2.9	0.276	0.33
Big Muddy River								
N-18	10/14/2015 9:00	2.5	0.032	0.56	<0.050	0.86	0.119	0.189
Middle Fork Big Muddy River								
NH-06	10/14/2015 15:40	2.5	0.0094	0.29	<0.050	0.66	0.072	0.113
NH-23	10/14/2015 14:00	2.4	0.02	0.49	<0.050	0.84	0.049	0.108
Field Blank								
FB-3	10/14/2015 11:30	<2.0	<0.0003	<0.050	<0.050	<0.50	<0.0100	<0.0100

Analyte Codes:
CBOD5 – Carbonaceous Biochemical Oxygen Demand
Chla – Chlorophyll a
NO3 – Nitrate Nitrogen
NH3 – Ammonia Nitrogen
TKN – Total Kjeldahl Nitrogen
oP – ortho phosphorus
TP – Total Phosphorus
n/a – not analyzed

Table 3-5. Round 2 Field Measurement Results

Station	Collection Date Time	Dissolved Oxygen (mg/L)	Water Temperature (degC)
Middle Fork Big Muddy River			
NH-06	10/14/2015 15:45	4.81	16.4
NH-23	10/14/2015 14:00	6.56	15.2
Big Muddy River			
N-17	10/14/2015 10:00	8.36	16.6
N-18	10/14/2015 9:00	7.64	16.9
N-19	10/14/2015 8:00	7.76	16.8
Andy Creek			
NZN-10	10/14/2015 13:15	2.45	16.2
NZN-12	10/14/2015 11:30	6.79	13
NZN-15	10/14/2015 12:20	1.49	14

Table 3-6. Round 2 Channel Morphometry and Flow

Station	Date	Stream Width (ft)	Average Water Depth (ft)	Average Velocity (ft/s)	Water Area (ft2)	Discharge (ft3/s)
Middle Fork Big Muddy River						
NH-23	10/14/2015 14:30	73	4.38	0.01	320.10	5.97
NH-06	10/14/2015 14:30	80	2.78	0.00	222.00	0.00
Andy Creek						
NZN-12	10/14/2015 11:50	21	0.42	0.00	8.80	0.00
NZN-15	10/14/2015 12:25	28	0.89	0.03	25.00	0.69
NZN-10	10/14/2015 13:20	18	0.67	0.01	12.00	0.16
Big Muddy River						
N-17	10/14/2015 10:19	52	1.37	1.89	71.40	146.06

4 Sediment Oxygen Demand and Dissolved Oxygen Monitoring

Sediment oxygen demand and dissolved oxygen were measured at select locations representative of river conditions in each watershed during the first round of sampling. SOD respirometer chambers were installed in accordance with the QAPP, and DO measurements during SOD testing were manually recorded in the field notes for a period of 2 hours or until DO dropped by 2 mg/L or to zero mg/L. The data were used to calculate SOD rates for use in the DO modeling activities. The SOD rate results are presented in Table 4-1.

Dissolved oxygen (DO) readings were recorded in the morning and the afternoon at select locations using optical dissolved oxygen sensors. The DO sensors were calibrated every morning on the days of sampling using the percent air saturation method in accordance with the manufacturer's operation manual.

The diurnal DO data are presented in Table 4-2.

Table 4-1. Sediment Oxygen Demand

Date	Site ID	Location	SOD, g/m2/day @ 20c (2)
9/22/2015	NH-07	Middle Fork Big Muddy River	-0.3789
9/22/2015	NH-23	Middle Fork Big Muddy River	-1.8326
9/23/2015	NZN-15	Andy Creek	-0.6979
9/24/2015	NG-02	Lake Creek	-1.4260
9/24/2015	NGA-02	Pond Creek	-0.8503
9/23/2015	N-19	Big Muddy River	-2.3607

Table 4-2. Diurnal Dissolved Oxygen Measurements

Station	Collection Date Time	Dissolved Oxygen (mg/L)
Middle Fork Big Muddy River		
NH-06	9/22/2015 12:18	12.03
NH-06	9/22/2015 18:15	13.32
NH-23	9/22/2015 14:30	7.91
NH-23	9/22/2015 17:53	9.75
Big Muddy River		
N-17	9/23/2015 7:32	7.43
N-17	9/23/2015 14:20	8.58
N-19	9/23/2015 17:30	8.05
Andy Creek		
NZN-15	9/23/2015 9:36	2.15
NZN-15	9/23/2015 12:20	1.94
Pond Creek		
NG-02	9/24/2015 8:44	7.54
NG-02	9/24/2015 8:45	7.35
NG-02	9/24/2015 9:27	7.08
NG-02	9/24/2015 14:19	14.77
Lake Creek		
NGA-02	9/24/2015 7:52	7.01
NGA-02	9/24/2015 14:54	6.75
NGA-02	9/24/2015 15:00	7.49
NGA-02	9/24/2015 15:27	8.83

5 Quality Assurance Review

A review was conducted to assess the quality and usability of data generated from implementation of the work activities and to assess adherence to protocols specified in the QAPP. Field and laboratory methods were reviewed and found to be in accordance with the QAPP; however, certain changes to sampling and analysis activities were implemented that deviated from the sampling plan presented in the QAPP and are documented in this section. Field measurement data and laboratory analytical data were verified and validated in accordance with the QAPP.

Overall, the data generated are of satisfactory quality and suitable for the intended uses, which include stream characterization and modeling for TMDL development. Some of the data, though acceptable for use, are qualified because of deficiencies in field or laboratory quality control procedures or conditions. Other data, though not specifically flagged with a data qualifier, are associated with uncertainties that prompt caution in their use. These are discussed in this section.

The following subsections of this document present the deviations, deficiencies and cautions associated with the data generated during the investigations. These subsections include the sampling plan changes implemented during the course of the investigation and the results of the data verification and data validation activities.

5.1 Changes from Sampling Plan (QAPP)

The QAPP was approved in September 2014 and contains the sampling plan for the investigations described in this report. Sampling was originally scheduled to occur during 2014 but was delayed a year because of unsuitably high flow conditions in the Upper Big Muddy River system. During this period of delay and prior to the sampling and analysis activities conducted in 2015, certain changes were made to the sampling plan or sampling protocols specified in the QAPP as noted in the following list. The QAPP was not updated to reflect these changes which are instead documented in this section of this report.

- The laboratory was changed to TriMatrix (and GLEC) from Brighton Analytical. The change in laboratories resulted in a change in reporting limits for ammonia (from 0.01 to 0.05 mg/L) and total Kjeldahl nitrogen (from 0.1 to o.5 mg/L). The reporting limits used for data validation are included in Table 5-2 of this report. These reporting limit changes did not affect the usability of the data for the Stage 3 modeling activities.
- Chlorophyll a analyses were added to evaluate possible effects of phytoplankton on dissolved oxygen levels.
- It was planned that nitrate be dropped from the analytical list as it is not essential for the Stage 3 modeling activities; however, it was analyzed for the second sampling event conducted in October 2015. The omission of nitrate analysis for the first sampling event in September 2015 does not affect the usability or completeness of the data.

- Changes in sampling locations occurred as NH-24 and N-18 were not accessible during Round 1 and NH-24 was not accessible during round 2, but N-18 was. Inaccessibility was caused by locked access gates with no trespassing signs and unavailability of contact personnel to gain access.
- The low flow condition threshold was exceeded for the Big Muddy River during both sampling rounds but sampled tributaries to the Big Muddy River were at acceptable low flow conditions.
- SOD measurements were moved from the planned location of NH-06 to the alternate location of NH-07 because there was no safe access to the main channel river banks at NH-06. In addition, SOD measurements were moved from the planned location of N-17 to the alternate location of N-19 because of inability to properly seat the respirometers at the N-17 location related to the presence of cobbles in the river bottom sediments that were at accessible wading depths.

5.2 Data Verification and Validation

The data generated are of overall good quality and acceptable for use with some qualifications as discussed below.

Completeness. The completeness criterion of 90% in the QAPP was met. One station (NH-24) out of 20 (26 stations total, if repeat visits counted) was not sampled during both events because of lack of access. All other locations were sampled with 100% analysis of samples submitted to the laboratory.

Accuracy and Precision. All quality control results for accuracy (method blank, lab control samples) and precision (lab and field duplicates) were within the control limits stated in the QAPP.

Representativeness. Representativeness was achieved through the use of standard operating procedures for sample collection and handling activities and laboratory analysis and reporting activities.

Discharge data. All stream discharge results are acceptable for use. Discharge was not measured at locations that were unsafe to wade or had no bridge access. These included N-17, N-18 and N-19 during the first sampling event. N-17 flows could not be measured from the bridge because of an equipment failure, while wading techniques at all three stations couldn't be employed because of unsafe water velocities, depths and/or mucky bottoms. N-17 flow measurements were successfully obtained during the second sampling event.

Laboratory QC data. All sample analytical results are acceptable for use.

- The holding time of 24 hours from sample collection to sample filtration was slightly exceeded for event 1 chlorophyll a analyses of NZN-15 (and DUP-1), FB-2, and NG-02 (and DUP-2) and for event 2 chlorophyll a analyses of N-18; however, the results for these samples are considered acceptable for their planned use.
- The matrix spike (MS) or matrix spike duplicate (MSD) recovery, but not both, was outside the control limits for the round 1 event ortho phosphorus analysis of NZN-15 and the round 2 event total kjeldahl nitrogen analysis in N-18. In both cases, the MS/MSD relative percent difference (RPD) was within the control limit. No action is required for deficient MS results and the sample results are considered acceptable for the planned use.
- The calibration reporting limit standard (CRL) recovery was outside control limits for the 10/14/2015 samples analyzed for nitrate, ammonia and total phosphorus. The method QC was within the limits. CRL recovery issues are not a cause for qualification per the method.

Field QC data. Field quality control (QC) samples were collected to assess bias associated with field and laboratory methods. The field QC samples included three rinse blank samples and three field duplicate sample pairs. The results of these analyses are presented below.

- **Rinse Blanks.** All field rinse blank sample results were below the detection limit with the exception of ammonia at 0.2 mg/L in the FB-1 sample collected at 9/22/2015 at 11:15. This ammonia result most likely did not impact the NH-07 sample collected at 9/22/2015 at 11:20. All samples were collected after cleaning the sample collection bucket by employing a detergent wash followed by a distilled water triple rinse, followed by a sample water rinse immediately prior to collection of the stream water sample. Based on the sample equipment cleaning procedures, it is unlikely that cross-contamination occurred in any environmental sample.
- **Duplicates.** The duplicate results were all acceptable with relative percent differences below the precision criterion (20%) specified in the QAPP. The duplicate sample quality assurance results are presented in Table 5-1. For the purposes of submitting field duplicate results in accordance with IEPA-formatting requirements for the Station Code field, one minute was added to the sample collection time to distinguish between duplicate samples, as approved by the IEPA project manager.

Table 5-1. Field Duplicate Pair Sample Results

Sample ID	$CBOD_5$ (mg/L)	Chl a	NH3 (mg/L)	NO3 (mg/L)	TKN (mg/L)	oP (mg/L)	TP (mg/L)
Round 1 Results							
NZN-15	<2	0.00352	0.47	n/a	1.2	0.214	0.245
DUP-1 (NZN-15)	<2	0.0046	0.45	n/a	1.1	0.187	0.229
RPD (%)		6.7	1.1	n/a	2.2	3.4	1.7
NG-02	5	0.03452	<0.05	n/a	0.84	<0.01	0.132
DUP-2 (NG-02)	5.4	0.03874	<0.05	n/a	1.1	<0.01	0.132
RPD (%)	1.9	2.9			6.7		0.0
Round 2 Results							
NZN-12	<2.0	n/a	<0.050	<0.050	0.51	0.115	0.154
DUP-3 (NZN-12)	<2.0	n/a	<0.050	<0.050	0.52	0.114	0.162
RPD (%)					0.5	0.2	1.3

*RPD= |S-D| x100 / (S+D)/2 where S: original sample; D: Duplicate sample
n/a – not analyzed

Conformance to Data Quality Objectives. Overall, the data generated during the investigation conformed to the project data quality objectives (DQOs) and are suitable for their intended uses. The monitored parameters were evaluated in terms of minimum measurement criteria, minimum measurement objectives, required detection limits, accuracy, precision and completeness using the DQOs presented in the project QAPP. Table 5-2 summarizes the results of the DQO quality assurance (QA) check.

The QA check shows apparent deficiencies with reporting limits for NH3, TKN and TP results; however, the values reported are subject to laboratory capabilities and also are deemed satisfactory for the intended use of the data. The completeness criteria reflect the number of samples and measurements that were originally planned; however, as noted previously, one location (NH-24) on private property was unable to be accessed and an alternate location is not available.

Table 5-2. Measurement Objectives and Criteria Check

					Matrix Spike/Matrix Spike Duplicate *				Lab Control Sample *			
Parameter	**Minimum Measurement Criteria**	**Minimum Measurement Objectives**	**Method *; MDL/Reporting Limit[1]**	**QA Check ****	**Accuracy (% recovery)**	**QA Check ****	**Precision (RPD)**	**QA Check ****	**Accuracy (% recovery)**	**QA Check ****	**Completeness**	**QA Check ****
Dissolved Oxygen	NA	0.1 mg/L[S]	Optical sensor; 0.1 mg/l [S]	Sat	NA	NA	NA	NA	NA	NA	90%	92.3%
Water Temperature	NA	0.1 degree C[S]	Thermometer; 0.1 degree C [S]	Sat	NA	NA	NA	NA	NA	NA	90%	92.3%
Ammonia	15.0 mg/L[G]	3.0 mg/L	SM4500NH3G; 0.009 mg/l / 0.01 mg/l	Sat (RL=0.05 mg/l)	80-120%	Sat	20%	Sat	80-120%	Sat	90%	92.3%
Total Kjeldahl Nitrogen	No Standard		EPA 351.2; 0.09 mg/l / 0.1 mg/l	Sat (RL=0.5 mg/l)	80-120%	Sat	20%	Sat	80-120%	Sat	90%	92.3%
Nitrate	No Standard		EPA 300.0 0.005 mg/l / 0.05 mg/l	Sat	80-120%	Sat	20%	Sat	80-120%	Sat	90%	NA***
Total Phosphorus	0.05 mg/L[G]	0.01 mg/L	SM4500PE; 0.008 mg/l / 0.01 mg/l	Sat (RL=0.01 to 0.02 mg/l)	80-120%	Sat	20%	Sat	80-120%	Sat	90%	92.3%
Ortho phosphorus	No Standard		SM4500PE; 0.008 mg/l / 0.01 mg/l	Sat	80-120%	Sat	20%	Sat	80-120%	Sat	90%	92.3%
$cBOD_5$	No Standard		SM5210B; NA / 2 mg/l	Sat	NA	NA	20%[a]	Sat	N/A	Sat	90%	92.3%
Chlorophyll a	No Standard		SM10200H 0.0003 mg/l / 0.0007 mg/l	Sat	80-120%	Sat	20%	Sat	80-120%	Sat	90%	92.3%

NA = Not Applicable
S = Required sensitivity
SM - Standard Methods of the Examination of Water and Wastewater, 20th Edition
EPA - EPA Methods for Chemical Analysis of Water and Wastes, March 1983
* = Limits reported in the QAPP are subject to change based upon capabilities of the contract lab
1 = Method Detection Limit (MDL) from SM and EPA.
G = State of Illinois General Use Water Quality Standard
[a] = Precision will be evaluated using laboratory replicates rather than MS/MSD
** = These columns document the results of the QA review and changes in the laboratory reporting limits (RL)
Sat = QA check is satisfactory, criterion met
***Nitrate is not an essential analyte for the Stage 3 modeling

6 References

Illinois Environmental Protection Agency (IEPA). 2012. *Illinois Integrated Water Quality Report and Section 303(D) List, 2012.* Clean Water Act Sections 303(d), 305(b) and 314 Water Resource Assessment Information and List of Impaired Waters Volume I: Surface Water. Bureau of Water, Division of Water Pollution Control. Springfield, Illinois.

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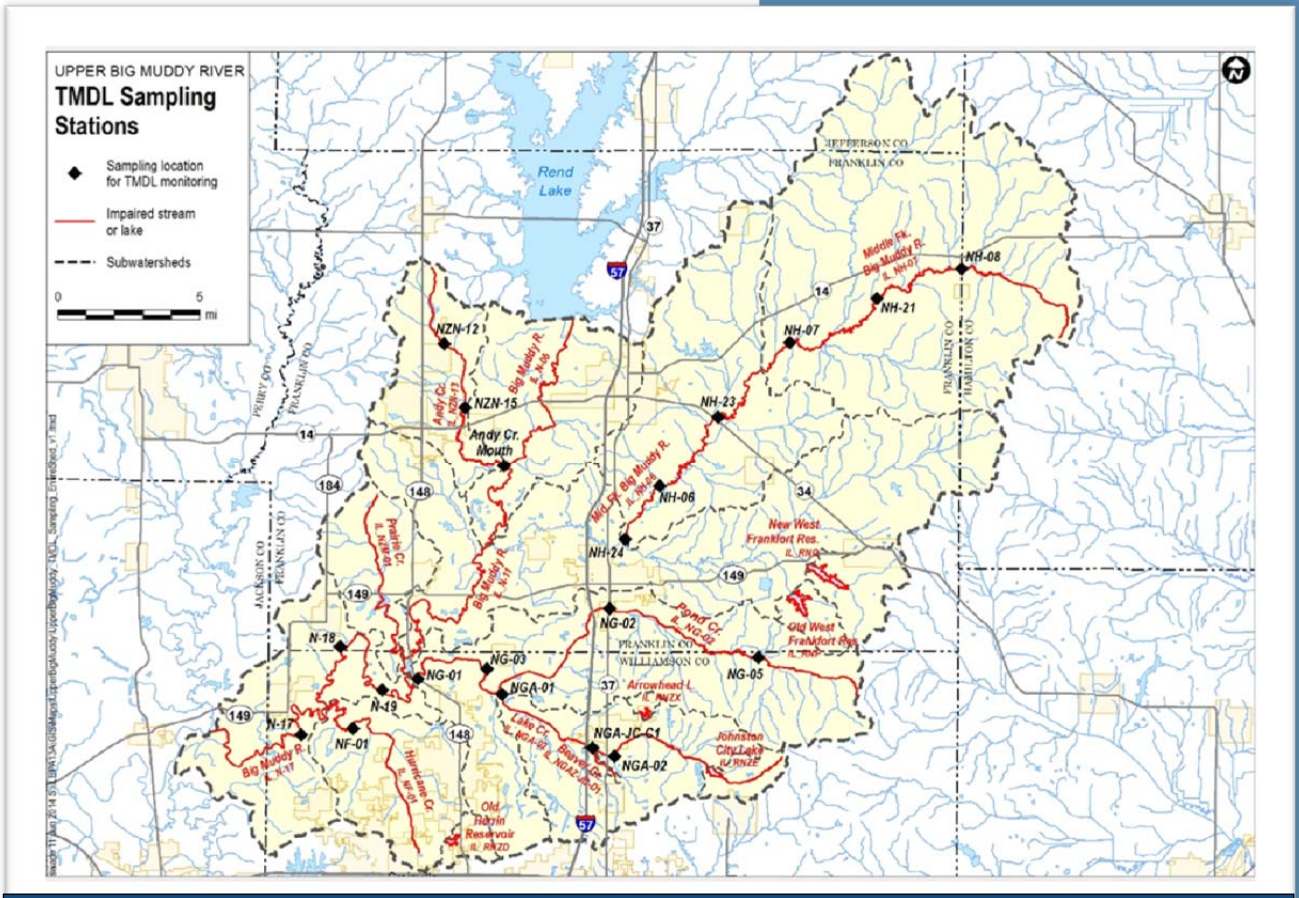
Attachment 1



Quality Assurance Project Plan

for TMDL Sampling Activities in the Upper Big Muddy River Watershed, Illinois

Prepared for:
Illinois Environmental Protection Agency

September, 2014

Project Contact:
David Dilks (734) 332-1200,
ddilks@limno.com

LimnoTech
Water Environment | Scientists Engineers

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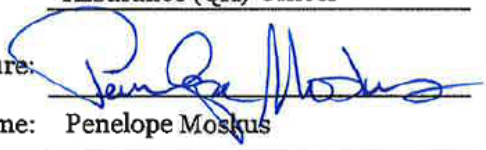
APPROVAL SHEET

Signature:		Date:	9-11-2014
Name:	David Dilks		
Title:	Project Administrator, Quality Assurance (QA) Officer	Affiliation:	LimnoTech
Signature:		Date:	9-11-14
Name:	Penelope Moskus		
Title:	Project Manager	Affiliation:	LimnoTech
Signature:		Date:	9-11-14
Name:	Abel Haile		
Title:	Supervisor, Watershed Management Section	Affiliation:	Illinois Environmental Protection Agency
Signature:		Date:	9/9/14
Name:	Michelle Rousey		
Title:	Bureau of Water QA Officer	Affiliation:	Illinois Environmental Protection Agency
Signature:		Date:	
Name:			
Title:		Affiliation:	
Signature:		Date:	
Name:			
Title:		Affiliation:	

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1 Project Management (Group A)

The purpose of the Quality Assurance Project Plan (QAPP) is to document the necessary procedures required to assure that the project is executed in a manner consistent with applicable United States Environmental Protection Agency (U.S. EPA) guidance documents and with generally accepted and approved quality assurance objectives. In this QAPP, U.S. EPA QAPP Guidance Group A requirements are discussed in this section (Section 1), Group B requirements are discussed in Section 2, Group C requirements are discussed in Section 3 and Group D requirements are discussed in Section 4.

This QAPP was prepared to support surface water sampling activities related to the development of Total Maximum Daily Loads (TMDLs) for impaired water bodies in the Upper Big Muddy River watershed:

This QAPP provides guidance and specifications to assure that:

- proper preventive maintenance, equipment calibration, and approved analytical protocols will be implemented so that all field measurements and sampling analytical results will be valid;
- sampling is conducted using sample tracking systems and chain-of-custody procedures which properly identify samples being collected and ensure the control of those samples from field collection through analysis and data reduction;
- records are produced and retained to document the quality of samples collected and analyzed, the validity of applied procedures, and the completeness of the investigation in relation to the approved scope of the project;
- generated data is validated; and
- calculations, evaluations, and decisions completed or deduced during the execution of the study are accurate, appropriate, and consistent with the objectives of the investigation.

The requirements of this QAPP are applicable to the activities of all participants in the investigation. This QAPP will address all anticipated activities necessary to execute the investigation.

1.1. Distribution List (A3)

Each organization listed on the approval sheet will receive an electronic copy of this QAPP via email. Individuals taking part in the project may request additional copies of the QAPP from the LimnoTech project manager listed in the following section of this QAPP. LimnoTech will retain in the project files the original approved QAPP containing the Approval Sheet with signatures and dates.

1.2. Project Organization (A4)

LimnoTech of Ann Arbor, Michigan, and its subcontractor, Brighton Analytical L.L.C. (BA) of Brighton, Michigan, will conduct activities on behalf of the Illinois Environmental Protection Agency

in support of TMDL development for impaired water bodies. LimnoTech will maintain the technical responsibility for implementing the water quality sampling activities for the Upper Big Muddy River watershed. Brighton Analytical will provide analytical laboratory services for LimnoTech.

LimnoTech will coordinate activities with its subcontractor. The staff of LimnoTech and the laboratories will report to their respective team leaders and project managers for technical and administrative direction. Each staff member has responsibility for performance of assigned quality control duties in the course of accomplishing identified tasks. The quality control duties include:

- completing the assigned task in a quality manner in accordance with the schedule and with established procedures.
- ascertaining that the work performed is technically correct and meets all aspects of the QAPP.

An organizational chart illustrating the study group hierarchy is presented in Figure 1. The roles, responsibilities and contact information of LimnoTech and other personnel that will work on this project are summarized in Table 1.

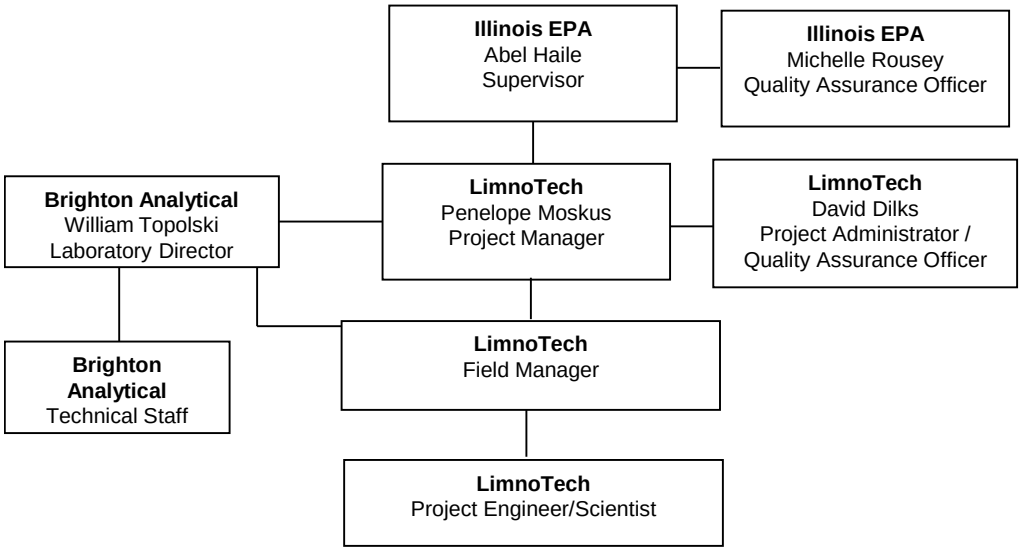

Figure 1. Study Organizational Chart

Table 1. Project Organization/Responsibilities/Contact List

Affiliation/Role	Personnel / Contact Information	General Responsibilities
Illinois EPA Supervisor	Abel Haile 217-782-3362 / abel.haile@illinois.gov	Review and approve all work products
Illinois EPA Quality Assurance Officer	Michelle Rousey 217-785-3944 / Michelle.rousey@illinois.gov	QAPP review
LimnoTech Project Administrator, Quality Assurance Officer	David Dilks 734-332-1200 / ddilks@limno.com	General and QA oversight; Review all work products
LimnoTech Project Manager	Penelope Moskus 734-332-1200 / pmoskus@limno.com	Project management; Direct all field, data evaluation, and reporting activities
LimnoTech Field Manager	Robert Betz 734-332-1200 / bbetz@limno.com Or Cathy Whiting 734-332-1200 / cwhiting@limno.com	Supervise all field sampling, field safety and health, quality assurance, data evaluation, and reporting activities
LimnoTech Project Engineer/Scientist	Chris Behnke 734-332-1200 / cbehnke@limno.com Cullen O'Brien 734-332-1200 / cobrien@limno.com	Field and technical support
Brighton Analytical L.L.C.	William Topolski 810-229-7575 / bai-brighton@sbcglobal.net	Laboratory analysis of field samples

*Note: The LimnoTech field manager and Project Engineer/Scientists change depending on staff availability at the time of field sampling.

The roles and responsibilities presented in Table 1 are further described below.

Illinois EPA Supervisor. The IEPA supervisor is responsible for the ensuring compliance with the overall goals of the project and will review and approve all work products.

Illinois EPA Quality Assurance Officer. The IEPA QA officer is responsible for reviewing and approving the QAPP, to ensure the project will produce quality results that meet the goals of the project.

LimnoTech Project Administrator/Quality Assurance Officer. The LimnoTech project administrator/QA officer is responsible for the overall administration and ensuring staff availability for the project. As part of the quality assurance and quality control (QA/QC) responsibilities, the project administrator will:

- Provide for overall direction of project objectives and activities;
- Provide for QA/QC management of all aspects of the project within the stated scope of responsibility;
- Approve reports and other materials for release to members of the project team and other external organizations.

LimnoTech Project Manager. The LimnoTech project manager is responsible for maintaining a clear definition of and adherence to the scope, schedule, and budget of the project. As a part of this responsibility, the project manager will:

- Serve as the communication link with the project team members and client;
- Direct all work performed by the organization and its subcontractors;
- Perform final review of field data reductions, report submittals, and presentations;
- Assure corrective actions are taken for deficiencies noted during project activities;
- Maintain budgetary and schedule surveillance of the work.

LimnoTech Field Manager. The LimnoTech field manager will be a project engineer or scientist and is responsible for implementing field activities, initial data acquisition, health and safety aspects of field activities, and for the proper selection and execution of procedures that have been accepted for use in the investigation. As part of the QA/QC responsibilities, the field manager will:

- Supervise project engineers/scientists executing data gathering tasks;
- Supervise the collection of samples so that sampling remains representative of actual field conditions;
- Supervise the regular maintenance of equipment to prevent unnecessary equipment failures and project delays caused thereby;
- Review the effectiveness of procedures and suggest changes that will enhance or more efficiently accomplish the objectives of the investigation;
- Prepare and review field data reductions, reports, submittals, and presentations to assure that data and conclusions accurately reflect observed conditions in the field;
- Assist in the maintenance of budgetary and scheduling surveillance.
- Communicate with the Brighton Analytical Laboratory Director regarding arrival of samples and laboratory analysis.

LimnoTech Project Engineer/Scientist. The assistant project engineer/scientist is responsible for the assisting in the implementation of field activities, initial data acquisition, health and safety aspects of field activities, and for the proper selection and execution of procedures that have been accepted for use in the investigation. As part of the QA/QC responsibilities, the assistant project engineer/scientist will:

- Perform data gathering and compilation tasks;
- Assist in reviewing the effectiveness of procedures and suggest changes that will enhance or more efficiently accomplish the objectives of the investigation;
- Assist in the collection of samples so that sampling remains representative of actual field conditions;
- Perform regular maintenance and calibration of equipment to prevent unnecessary equipment failures and project delays caused thereby;
- Assist in the preparation and review of field data reductions, reports, submittals, and presentations to assure that data and conclusions accurately reflect observed conditions in the field.

Brighton Analytical Laboratory Director. The laboratory director will ensure strict adherence to all protocols in the QAPP, will direct the Brighton Analytical technical staff, and notify the LimnoTech project manager in advance of any deviations to QA protocols, and will work with the LimnoTech project manager to resolve any laboratory QA/QC issues.

Brighton Analytical Laboratory Technical Staff. The laboratory technical staff will:

- Perform analytical procedures;
- Supply sampling containers and shipping cartons;
- Maintain laboratory custody of samples; and
- Strictly adhere to all protocols in the QAPP.

1.3. Problem Definition/Background (A5)

The project activities associated with this QAPP will include surface water sampling activities to provide data that will be used to support development of TMDLs for impaired water bodies in the Upper Big Muddy River watershed.

Section 303(d) of the 1972 Clean Water Act requires States to define impaired waters and identify them on a list, which is referred to as the 303(d) list. The State of Illinois has finalized the 2012 303(d) list (IEPA, 2012), which is available on the web at http://www.epa.state.il.us/water/tmdl/303d-list.html. The Clean Water Act requires that a TMDL be completed for each pollutant listed for an impaired water body. TMDLs are prepared by the States and submitted to the U.S. EPA for approval. In developing the TMDL, a determination is made of the greatest amount of a given pollutant that a water body can receive without exceeding water quality standards and designated uses, considering all known and potential sources. The TMDL also takes into account a margin of safety, which reflects scientific uncertainty, as well as the effects of seasonal variation.

As part of the TMDL process, the Illinois Environmental Protection Agency (IEPA) and several consultant teams compiled, reviewed and evaluated the sufficiency of available data to support TMDL development for the Upper Big Muddy River watershed. The data review included:

- confirmation of the impairments identified on the 303(d) list,
- further identification of potential sources causing these impairments,
- identification, description and recommendations for methodologies, procedures and/or models to be used in the development of TMDLs, and
- recommendations for additional data needed to support the modeling, where necessary, along with general data collection plans

The additional data collection work approved by Illinois EPA is presented and described in the following subsection of this QAPP.

1.4. Project/Task Description (A6) and Schedule

Monitoring will be conducted within the Upper Big Muddy watershed in southern Illinois. Table 2 summarizes the scope of work. The sampling sites and coordinates are presented in Table 3 and depicted on Figures 1 and 2. All sampling activities will be conducted in accordance with standard operating procedures (SOPs) presented in Appendix A.

Stream Surveys. Stream sampling surveys will be conducted during low to medium flow conditions, as specified in Table 2. Survey deployment decisions will be based on real-time streamflows at United States Geological Survey (USGS) gages in or near the watershed. Low to medium flow surveys will be targeted for dry conditions and periods when the real-time streamflow of the nearest gage is in the vicinity of the 20th percentile flow value, based on the period of record data. If necessary, low to medium flow surveys may be conducted at slightly higher flows, when the real-time streamflows are in the vicinity of or less than the 50th percentile flow value. Tributary monitoring will be conducted if the tributaries are flowing. The USGS gages and daily mean flow statistics are presented in Table 4.

Surface Water Quality Sampling. Water quality grab samples and water quality measurements will be collected at mid-stream or at the location where maximum flow is observed, where safely practicable. Grab samples will be collected from bridges, where possible, preferably using weighted bottle, dip or direct samplers attached to a pole or a line. Sampling equipment will be decontaminated between locations using a river water rinse followed by a triple deionized water rinse following the SOP for Equipment Cleaning presented in Appendix A. Water quality samples will be stored in an iced cooler prior to and during overnight express shipment to the analytical laboratory following strict chain-of-custody procedures as specified in the Sample Handling, Packing and Shipping SOP presented in Appendix A. The samples will be analyzed for five day carbonaceous biochemical oxygen demand ($cBOD_5$), ammonia (NH_3), nitrate (NO_3), total kjeldahl nitrogen (TKN), total phosphorus (TP) and ortho-phosphorus (oP) as specified for the different watershed surveys in Table 2.

Surface Water Measurements. Field water quality measurements (i.e., water temperature, dissolved oxygen (DO)) will be recorded using instruments (e.g., YSI or Hydrolab meters) that are calibrated daily in accordance with manufacturer recommendations. Channel morphometry/stream depth, and water velocity measurements will be conducted in accordance with the SOP for Surface Water Flow Measurements in Appendix A. Locations will be selected for channel morphometry/stream depth and water velocity measurements based on two factors: 1) is it a good site for flow calculation; and 2) are the sites spaced out throughout the watershed. Sediment oxygen demand (SOD) and continuous DO measurements (or morning and afternoon DO measurement) will be conducted in accordance with the SOPs for Sediment Oxygen Demand Measurements and Field Water Quality Measurements, respectively, presented in Appendix A. Locations for SOD measurements will be selected in the field, and will be representative of conditions in the river.

Schedule. An example schedule for implementation of data collection activities is presented in Table 5. Field activities will commence within two weeks after Illinois EPA communicates approval of the QAPP and approval to proceed, subject to the sampling requirements (i.e., discharge level and precipitation conditions) being met for each watershed. It is anticipated that all dry weather low or medium flow events will be conducted before the fall wet weather season. Available USGS surface water discharge gages in or near the watersheds will be monitored to determine the occurrence of appropriate flow levels for field deployment. The schedule will be updated as necessary and will be used by the Project Manager to review overall progress of the project.

Table 2. Scope of Work, Upper Big Muddy Watershed

Waterbody Name & Segment	Sampling Station ID	Work Description
Middle Fork Big Muddy River Segment IL_NH-06	3 locations • NH-06 • NH-23 • NH-24	2 low-to-medium flow surveys to measure: • CBOD5, ammonia, nitrate, total phosphorus, ortho-phosphorus • DO, temperature, channel morphometry, velocity, depth and flow 1 low-to-medium-flow survey to measure: • SOD and continuous DO (at 1 location in segment IL_NH-06) • TKN at NH-24

Waterbody Name & Segment	Sampling Station ID	Work Description
Middle Fork Big Muddy River Stream Segment IL_NH-07	3 locations • NH-07 • NH-08 • NH-21	1 low-to-medium flow survey to measure: • CBOD5, ammonia, nitrate, total phosphorus, ortho-phosphorus • DO, temperature, channel morphometry, velocity, depth and flow 1 low-to-medium-flow survey to measure: • SOD and continuous DO (at 1 location in segment IL_NH-07) • TKN at NH-07
Andy Creek Segment IL_NZN-13	3 locations • NZN-12 • NZN-15 • unnamed location near mouth.	2 low-to-medium flow surveys to measure: • CBOD5, ammonia, nitrate, total phosphorus, ortho-phosphorus • DO, temperature, channel morphometry, velocity, depth and flow 1 low-to-medium-flow survey to measure: • SOD and continuous DO (at 1 location in segment IL_NZN-15) • TKN at unnamed location near mouth
Big Muddy River Segment IL_N-17	3 locations • N-17 • N-18 • N-19	1 low-to-medium flow survey to measure: • CBOD5, ammonia, nitrate, total phosphorus, ortho-phosphorus • DO, temperature, channel morphometry, velocity, depth and flow 1 low-to-medium-flow survey to measure: • SOD and continuous DO (at 1 location in segment IL_N-17) • TKN at N-19
Hurricane Creek Segment IL_NF-01	1 location • NF-01	1 low-to-medium flow survey to measure: • CBOD5, ammonia, nitrate, total phosphorus, ortho-phosphorus • DO, temperature, channel morphometry, velocity, depth and flow
Pond Creek Segment IL_NG-02	4 locations • NG-01 • NG-02 • NG-03 • NG-05	1 low-to-medium flow survey to measure: • CBOD5, ammonia, nitrate, total phosphorus, ortho-phosphorus • DO, temperature, channel morphometry, velocity, depth and flow 1 low-to-medium-flow survey to measure: • SOD and continuous DO (at 1 location in segment IL_NG-02) • TKN at NG-01

Waterbody Name & Segment	Sampling Station ID	Work Description
Lake Creek **Segment IL_NGA-02**	3 locations • NGA-01 • NGA-02 • NGA-JC-C1	1 low-to-medium flow survey to measure: • CBOD5, ammonia, nitrate, total phosphorus, ortho-phosphorus • DO, temperature, channel morphometry, velocity, depth and flow 1 low-to-medium-flow survey to measure: • SOD and continuous DO (at 1 location in segment IL_NGA-02) • TKN at NGA-01

Table 3. Sampling Locations

Stream	Access	TMDL Station ID	Longitude	Latitude
Upper Big Muddy River Watershed				
Mid Fork Big Muddy	Deering Road/Co. Hwy. 5	NH-06	-88.89984	37.9492
Mid Fork Big Muddy	Illinois State Hwy. 34	NH-23	-88.86243	37.98601
Mid Fork Big Muddy	Unnamed lane west of Deering Road/Co. Hwy. 5 at W. Neal Rd	NH-24	-88.92182	37.92129
Mid Fork Big Muddy	Macedonia Road/Co. Hwy. 18/Co. Hwy 34	NH-08	-88.70546	38.06443
Mid Fork Big Muddy	N. Thompsonville Road/Co. Hwy. 17	NH-21	-88.76022	38.04862
Mid Fork Big Muddy	Bessie Road/Co. Hwy. 2	NH-07	-88.81642	38.02531
Andy Creek	Satch Road	NZN-15	-89.025722	37.990222
Andy Creek	Park Street Rd/Co. Hwy. 37	NZN-12	-89.0395556	38.0236111
Andy Creek	Forest cut/path north of Yellow Banks Road/Co. Hwy. 11 and west of Big Muddy River	No previous ID	-89.00024077	37.95960821
Big Muddy River	Cambria Road/Co. Hwy. 9	N-17	-89.1295	37.81761
Big Muddy River	Pump Station Road/Lane	N-18	-89.10472	37.86389
Big Muddy River	Unnamed lane north of Clifford Road at Big Muddy Road	N-19	-89.07769	37.84137
Hurricane Creek	N. Bend Road	NF-01	-89.09622	37.8211
Pond Creek	Illinois State Hwy. 148	NG-01	-89.05473	37.84728
Pond Creek	Freeman Spur Road	NG-03	-89.0102	37.85276
Pond Creek	Illinois State Hwy. 37	NG-02	-88.93162	37.88491
Pond Creek	Liberty School Road	NG-05	-88.835472	37.859722
Lake Creek	Stiritz Road	NGA-01	-89.00055	37.83961
Lake Creek	Binkley Road	NGA-02	-88.92765	37.80754
Lake Creek	Prosperity Road/Co. Hwy. 1	NGA-JC-C1	-88.9420944	37.8116972

*Note that sampling locations may be changed if accessibility if the locations in Table 3 are inaccessible or located on private property, to avoid trespassing.

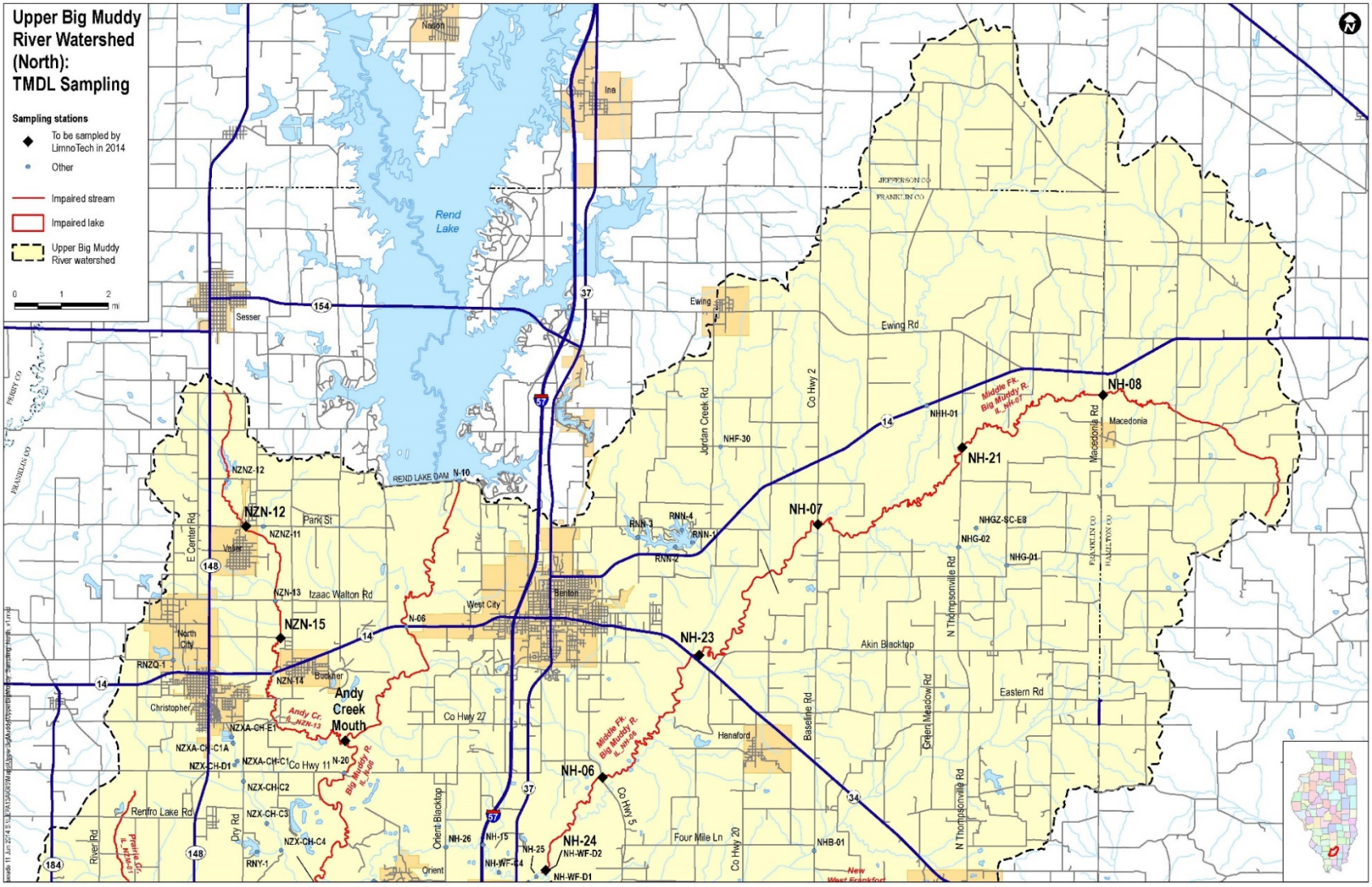

Figure 2. Upper Big Muddy River Watershed Sampling Locations (Northern Watershed)

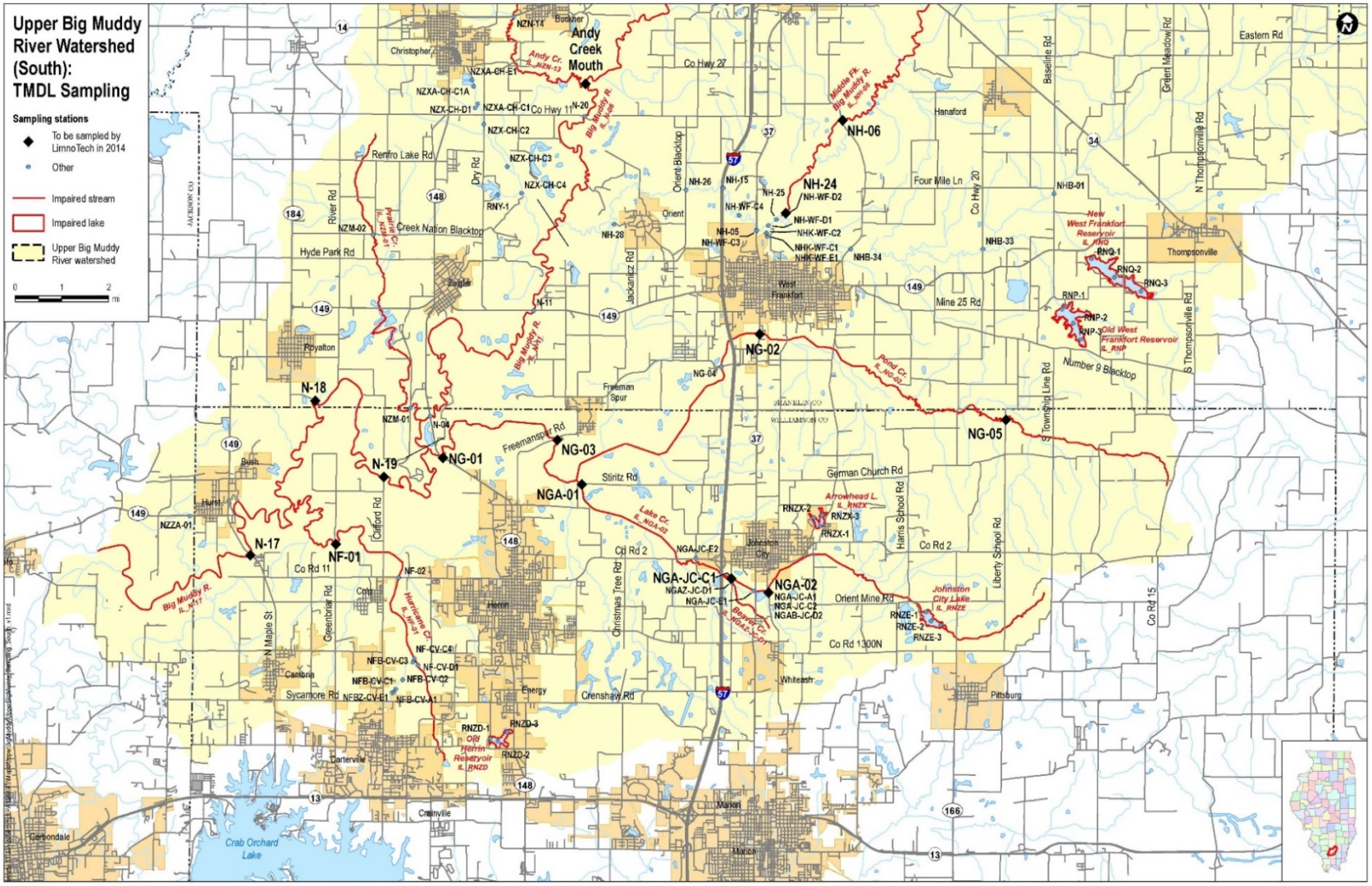

Figure 3. Upper Big Muddy River Watershed Sampling Locations (Southern Watershed)

Table 4. USGS Gage Streamflow Statistics

Watershed	Nearest USGS Gage	USGS Gage Number	Monthly 20th Percentile Flow (cfs)	Monthly 50th Percentile Flow (cfs)	Monthly 80th Percentile Flow (cfs)
Big Muddy	Big Muddy River at Pumfield, IL	05597000	Jul 107 Aug 63 Sep 50 Oct 38	Jul 347 Aug 171 Sep 89 Oct 54	Jul 647 Aug 365 Sep 206 Oct 148
Percentile values calculated from USGS website daily mean streamflow values for the period of record (Calculation Period 1970-10-01 -> 2013-09-30) The USGS real-time streamflow values for this gage can be accessed at the following URL: http://waterdata.usgs.gov/nwis/inventory?agency_code=USGS&site_no=05597000					

Table 5. Schedule

Event	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7
Approval to proceed from IL-EPA	**X**						
Upper Big Muddy River							
Survey 1 - low/medium flow							
Survey 2 - low/medium flow							

*This schedule is approximate, and contingent upon QAPP approval and appropriate flow conditions for sampling.

1.5. Quality Objectives and Criteria (A7)

A summary of the minimum measurement criteria and data quality objectives (DQOs) are presented in Table 6.

Precision

Precision is a measure of agreement among repeated measurements of the same property under identical, or substantially similar, conditions; calculated as either the range or as the standard deviation. Precision may also be expressed as a percentage of the mean of the measurements, such as relative range or relative standard deviation (coefficient of variation).

Precision will be measured in the laboratory during the analysis of matrix spike and matrix spike duplicate samples. A replicate aliquot will be analyzed for cBOD5 to assess precision instead of a spiked duplicate.

The analyses of the duplicate samples are considered acceptable if the calculated relative percent difference (RPD) of the measurements is within the acceptance limits listed in Table 6.

The results of the duplicate analyses are used to calculate the RPD for evaluating precision using the following formula:

$$RPD = [(A - B) / (A + B)/2] * 100$$

where:

A = Original sample concentration

B = Duplicate sample concentration

Bias

Bias is the systematic or persistent distortion of a measurement process that causes errors in one direction.

Accuracy

Accuracy is a measure of the overall agreement of a measurement to a known value. Accuracy includes a combination of random error (precision) and systematic error (bias) components that are due to sampling and analytical operations.

Accuracy will be measured during the analysis of environmental water by using laboratory control spike (LCS) samples. In the laboratory, samples of deionized water will be fortified (or spiked) with the analytes of interest. These LCS samples will be analyzed with each batch of samples. The analyses of the LCS samples are considered acceptable if the calculated concentrations for all analytes of interest are within the acceptance limits listed in Table 6.

The results of the spiked samples are used to calculate the percent recovery for evaluating accuracy using the following formula:

Percent Recovery = [(S - U) / T] * 100

where

S = Spiked sample concentration

U = Unspiked sample concentration

T = True spike concentration

Representativeness

Representativeness is the measure of the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition.

Representativeness of data will be ensured using established field and laboratory procedures and their consistent application. To aid in the evaluation of the representativeness of the sample data, field blank samples (including equipment rinse blank) and laboratory method blank samples will be evaluated for the presence of contaminants.

Comparability

Comparability is a measure of the confidence with which one data set or method can be compared to another.

Comparability will be maximized by using standard analytical methods and standardized, documented sampling techniques. Documentation will include all sampling locations, conditions, and field sampling methods. All results will be reported in standard units or, for field parameters, as defined in the method. All laboratory calibrations will be performed using standards traceable to the

National Institute for Standards and Technology (NIST) or another certified reference standard source.

Completeness

Completeness is a measure of the amount of valid data needed to be obtained from a measurement system.

The percent completeness is calculated by dividing the number of valid sample results by the total number of samples planned, and multiplying the result by 100 percent. Completeness will be reported as the percentage of all measurements judged valid. The following equation will be used to determine completeness:

$$\text{Percent Completeness} = (V/T) * 100$$

where

V = Valid number of sample results

T = Total number of samples planned

For this project, the QA objective for degree of completeness for both field and laboratory data is 90 percent. If completeness is less than the target of 90 percent the Project Administrator/Quality Assurance Officer will evaluate the data to determine whether there are enough data to complete the study or if additional data collection is necessary.

Sensitivity

Sensitivity is the capability of a method or instrument to discriminate between measurement responses representing different levels of the variable of interest.

Analytes measured for this project may be present in analytically low concentrations throughout the steams. All analytes are subject to chemical, biological, and physical processes that will alter their presence in the streams. It is the intent of this project to employ methods of measurements that will detect and quantify all analytes of interest wherever possible.

Although there are many intended and potential uses of the data, minimum measurement criteria will be established at the lowest analyte concentration required for planned uses of the measurement data. Minimum measurement criteria are State of Illinois water quality standards for general use waters where applicable. Where no minimum measurement criteria can be identified, the water samples will be analyzed to the lowest concentration readily achievable by the laboratory. The monitored parameters and the established minimum measurement criteria are shown in Table 6.

Table 6 also gives the minimum measurement objectives for the project. The minimum measurement objectives will be set at approximately one-fifth of the minimum measurement criteria shown to ensure that analytes will be measured with reasonable accuracy at the minimum measurement criteria concentrations, and measured to reasonable levels below the minimum measurement criteria.

The minimum measurement objective for any analyte will be achieved when the analytical procedure selected for sample analysis can be shown to have a method detection limit (MDL) at or below the minimum measurement objective. Table 6 compares the minimum measurement objective against the reporting limit achieved by Brighton Analytical. All analytes meet the minimum measurement objective.

Analyte MDLs shall be determined by the USEPA method given in the Code of Federal Regulations (CFR), Volume 40, Part 136, Appendix B. The MDL is defined as “the minimum concentration of a

substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte." Since the MDL procedure is based upon precision obtained for a standard greater than the MDL, it also is a measure of method sensitivity at concentrations near the MDL.

For analytes without minimum measurements criteria, the minimum measurement objectives will be understood to be the MDL level that is readily achievable using analytical methods generally employed at the IEPA laboratory. For parameters where MDLs are not applicable such as temperature and dissolved oxygen, the minimum measurement objectives shown in Table 6 are the sensitivity to be obtained by the measurement method. The accuracy, precision, and completeness for each parameter are also indicated in Table 6.

Table 6. Measurement Objectives and Criteria

					MS/MSD *	LCS *	
Parameter	**Minimum Measurement Criteria**	**Minimum Measurement Objectives**	**Method *; MDL/Reporting Limit[1]**	**Accuracy (% recovery)**	**Precision (RPD)**	**Accuracy (% recovery)**	**Completeness**
Dissolved Oxygen	NA	0.1 mg/L[S]	Optical sensor; 0.1 mg/l [S]	NA	NA	NA	90%
Water Temperature	NA	0.1 degree C[S]	Thermometer; 0.1 degree C [S]	NA	NA	NA	90%
Ammonia	15.0 mg/L[G]	3.0 mg/L	SM4500NH3G; 0.009 mg/l / 0.01 mg/l	80-120%	20%	80-120%	90%
Total Kjeldahl Nitrogen	No Standard		EPA 351.2; 0.09 mg/l / 0.1 mg/l	80-120%	20%	80-120%	90%
Nitrate	No Standard		EPA 300.0 0.005 mg/l / 0.05 mg/l	80-120%	20%	80-120%	90%
Total Phosphorus	0.05 mg/L[G]	0.01 mg/L	SM4500PE; 0.008 mg/l / 0.01 mg/l	80-120%	20%	80-120%	90%
Ortho-Phosphorus	No Standard		SM4500PE; 0.008 mg/l / 0.01 mg/l	80-120%	20%	80-120%	90%
$cBOD_5$	No Standard		SM5210B; NA / 2 mg/l	N/A	20%[a]	N/A	90%

NA = Not Applicable
S = Required sensitivity
* = Limits are subject to change based upon capabilities of the contract lab
1 = Method Detection Limit (MDL) from SM and EPA.
G = State of Illinois General Use Water Quality Standard
[a] = Precision will be evaluated using laboratory replicates rather than MS/MSD
SM - Standard Methods of the Examination of Water and Wastewater, 20th Edition
EPA - EPA Methods for Chemical Analysis of Water and Wastes, March 1983

1.6. Special Training/Certification (A8)

A variety of professional staff (engineers, scientists and others) will be involved in this monitoring program. Project staff will be assigned duties based on their qualifications to accomplish the task. The Project Manager will determine the appropriateness of an individual to undertake a task.

The Field Manager will be responsible for ensuring training sessions are carried out for all field staff on proper sampling, sample handling and shipping, and general field procedures prior to conducting the first sampling event. Specific emphasis will be placed on QA/QC issues as well as on health and safety. Field staff will receive a safety briefing conducted by Robert Betz of LimnoTech (Field Manager supervising sampling activities), with emphasis on field hazards and materials handling. Training will also include the operation, maintenance and calibration of field equipment, including multi-parameter probes, velocity meters, and all other on-site equipment used throughout the field program. SOPs for program elements will be distributed to appropriate staff and available at all times.

The laboratory will be responsible for training and certifications of laboratory personnel in accordance with the laboratory's quality assurance manual. All laboratory personnel will receive appropriate training and have proven proficiency in their designated analytical procedures. Laboratory personnel will be provided copies of the appropriate laboratory procedures, which will be available at all times.

1.7. Documents and Records (A9)

The LimnoTech project manager will ensure that the project team has the most current approved version of the QAPP. The project manager is responsible for initiating project files and for overseeing maintenance of the files during the course of the project. All project files will be properly identified by client, project name, project code and file description for all appropriate correspondence, memoranda, calculations, technical work products, and other project-related data. In addition, a quality assurance file will be maintained containing all QA/QC related information. A back up of all computer files containing important project information will also be maintained.

Documents generated by field activities may include staff notes, field logs, equipment logs, field on-site measurement data sheets, field audit reports and chain of custody forms. Documents generated by laboratory activities may include QA/QC documentation, laboratory bench sheets, laboratory results (expected turn-around time is two weeks from receipt of samples at the laboratory), and laboratory audit reports. These documents will be maintained in the project files.

At the conclusion of the project, all relevant information from the project files and computer disks will be archived. Documents will be retained for a minimum period of three years following archiving.

2
Data Generation and Acquisition (Group B)

The U.S. EPA QAPP Guidance Group B Data Generation and Acquisition elements (B1-B10) are addressed below.

2.1 Sampling Process Design (B1)

The sampling process design is presented in Sections 1.3 and 1.4 of this QAPP, including sampling rationale, locations, media, frequencies, and schedules.

2.2 Sampling Methods (B2)

Standard operating procedures (SOPs) will be employed to provide consistency and reproducibility to the sampling methods used by field personnel. The following sections present or reference the detailed methods for performing sampling activities including related support procedures for equipment cleaning, field measurements, and calibration and maintenance of field instruments. Sample custody procedures are presented in the Sample Handling and Custody Section of this QAPP.

2.2.1 Surface Water Sample Collection

Surface water grab samples will be collected as specified in the Section 1.4 and according to the procedures presented in Appendix A.

2.2.2 Stream Morphometric and Discharge Monitoring

Stream discharge monitoring will be conducted as specified in Section 1.4 and according to the procedures presented in Appendix A.

2.2.3 Field Water Quality Measurements and Monitoring

Instantaneous water quality measurements (e.g. temperature and DO) will be collected using field instruments according to the procedures presented in Appendix A. In-situ monitoring instruments and equipment will be installed in a manner using methods that incorporate the unique requirements of specific locations. The main concern will be the security of the instruments, equipment and generated data. Maintenance, cleaning and/or data download activities for in-situ instruments will be performed at a frequency necessary to assure that representative data are generated and recorded for transfer to the project files.

2.2.4 Cleaning of Equipment and Materials

All reusable equipment and materials used during the field activities will be cleaned prior to use at the site and at specified intervals during the field activities. Cleaning will be performed according to the procedures specified in Section 1.4 and as presented in Appendix A to avoid the introduction of any chemical constituents or cross-contamination to the soils or groundwater. Equipment and materials that may be used during the investigation include water and/or sediment sample collection devices.

Equipment cleaning will be performed using water from a source approved by the project manager. If needed, a designated cleaning or decontamination area will be used or constructed so that all water generated during cleaning operations will be contained for proper disposal.

2.3 Sample Handling and Custody (B3)

Sample handling will be performed so as to collect, store, submit to the laboratory and analyze representative samples using methods as specified in Section 1.4 and according to the procedures presented in Appendix A. Sample containers, volumes, preservatives and holding times are summarized in Table 7. Laboratory sample custody will be performed in accordance with the laboratory's Quality Assurance Manual

2.4 Analytical Methods (B4)

The following section details aspects of the analytical requirements, ensuring that appropriate analytical methods are employed. Table 6 summarizes the analytical methods to be used by the contract laboratory. Table 7 displays the required container type, sample volume, preservation, and holding time for each parameter according to the previously referenced methods. The laboratory will provide sample containers from a commercial supplier. All sample containers will be new and pre-cleaned by the supplier. In addition, the contract laboratory will provide sample labels for each bottle and add the required preservative for each parameter, where feasible.

The analytical data results and intra-laboratory QA/QC results will be submitted by the contract laboratory to the Field Manager or other designated contact person within a specified time frame from the completion of each sampling event.

In the event a new contract laboratory needs to be chosen, the LimnoTech project manager will contact the IEPA Supervisor to explain the need for a new laboratory and ensure the laboratory is capable of providing the services described in this QAPP.

Table 7. Guidelines for Sample Container Preparation and Preservation

Parameter	Container	Recommended Sample Volume	Preservation	Holding Time
TKN, NH_3, TP	Polyethylene	1000 ml	H_2SO_4, pH<2* Cool, ≤ 6° C	28 days
NO_3, oP	Polyethylene	1000 ml	Cool, ≤ 6° C	48 hours
$CBOD_5$	Polyethylene or Glass	1000 ml	Cool, ≤ 6° C	48 hours
*Sample containers with preservative added will be provided by the laboratory				

2.5 Quality Control (B5)

All field operations personnel are responsible for ensuring that proper procedures are followed for sample collection and handling, sample preservation, and sample custody of the delivered samples to the designated laboratory. If noncompliance issues arise, an investigation and corrective action report prepared by the responsible supervising field personnel will be submitted to the Project Manager. The accuracy and precision of all data measurements must be quantifiable. Analytical procedures used for data analysis must be performed according to approved standard methods. Data measurements

should be recorded in a controlled environment in which a quality control program can be maintained.

Field quality will also be assessed through the collection of field duplicate samples and equipment rinse blank samples. Field duplicates will be collected at a frequency of one for every group of 10 samples. Equipment rinse blank samples will be collected at a frequency of one for each day of sampling or one for every group of 20 samples.

The contract laboratory is responsible for implementing its QA/QC Manual, which is an internal quality assurance plan for laboratory procedures. The contract lab is responsible for the accuracy and reliability of analytical methods and final data reports. If noncompliance issues arise, an investigation and corrective action report will be prepared and submitted from the laboratory to the Project Manager. The contract lab is responsible for providing data qualifiers and/or case narratives to inform the Project Manager of any analytical exceptions that fall outside of routine method protocols. Analytical quality control will be performed in accordance with the laboratory QA/QC Manual, the specified analytical methods, and as discussed under the Quality Objectives and Criteria Section of this QAPP.

2.6 Instrument/Equipment Testing, Inspection, and Maintenance (B6)

All field and laboratory instruments/equipment shall be routinely maintained according to manufacturer instructions and accepted procedures associated with the selected analytical methods, SOPs and the laboratory's QA/QC Manual, as applicable. Field instruments and equipment shall be tested and inspected prior to sampling events. An adequate supply of spare parts shall be maintained as necessary for equipment maintenance.

2.7 Instrument/Equipment Calibration and Frequency (B7)

Calibration procedures for field and laboratory instruments/equipment will follow manufacturer instructions and accepted procedures in accordance with the selected analytical methods, standard operating procedures (SOPs) for field and laboratory activities and the laboratory's QA/QC Manual, as applicable. In order to maintain field precision and accuracy, field instruments will be calibrated to known standards. DO meter and continuous DO sondes will be calibrated to saturated air per manufacturer's instructions (see sections III and IV of Field Water Quality Measurements SOP in Appendix A).

Calibration frequency and preventative maintenance of field analytical equipment will be conducted according to the SOPs (see sections III and IV of Field Water Quality Measurements SOP in Appendix A). Laboratory instrumentation and equipment will follow manufacturer instructions and accepted procedures associated with the selected analytical methods, the laboratory's Standard Analytical Procedures (SAPs) (Appendix B) and Quality Assurance Manual (Appendix C).

2.8 Inspection/Acceptance of Supplies and Consumables (B8)

All supplies and consumables for field and laboratory activities will be inspected by the field operations teams and laboratory managers, respectively, to guarantee their usability. Supplies or consumables found to be deficient for the needs of the project will not be used.

2.9 Non-direct Measurements (B9)

Non-direct measurements will not be used in implementation of the monitoring program.

2.10 Data Management (B10)

Data generated through field and laboratory activities will be used for developing models and reports. Reporting formats will vary depending on the purpose for which the data has been assembled, but will include such items as field books, field calibration and measurement records, electronic data downloaded from field instruments, laboratory analytical results and QC reports. The Project Manager or designee has the responsibility of maintaining all documents and data generated during field programs and received from the laboratory. The Laboratory Technical Director has the same responsibility for laboratory data and information.

Field and laboratory documents will be kept in the project files. All electronic files will be backed up on a regular basis. At the conclusion of the project all relevant information, project files and electronic data will be turned over to the Project Manager. Paper and electronic files will be retained for a minimum period of three years following archiving.

3 Assessment and Oversight (Group C)

The U.S. EPA QAPP Guidance Group C Assessment and Oversight elements are addressed in this section.

3.1 Assessment and Response Actions (C1)

Internal quality control checks will be performed to ensure the field and laboratory generated measurements meet the project quality assurance objectives.

The LimnoTech Field manager is responsible for evaluating whether the sampling protocol is being followed. In addition the LimnoTech Project Manager will perform quality control checks on sample field data, including independent assessment of data entry and analyses. Quality control and noncompliance issues related to field activities will require an investigation and corrective action conducted under the supervision of the Project Manager.

The contract laboratory shall maintain internal quality assurance programs described in their quality assurance plans. When the possibility of quality control problems or noncompliance issues arise that may affect the usability of data, an investigation and corrective action will be conducted by the Laboratory Director and communicated to the Project Manager.

3.2 Reports to Management (C2)

Periodic summary reports will be prepared by the Project Engineer in charge of Quality Assurance, if necessary, to inform the Project Manager of the project status. The reports will include:

- Periodic assessment of measurement data accuracy, precision, and completeness;
- Results of performance audits and/or systems audits;
- Significant Quality Assurance/Quality Control problems and recommended corrective action;
- Status of corrective action implementation to any problems previously identified.

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4 Data Validation and Usability (Group D)

The U.S. EPA QAPP Guidance Group D Data Validation and Usability elements are addressed in this section. The purpose of these elements is to determine if the data meet the project's Data Quality Objectives (validation) and to evaluate the data against the method, procedural and/or contractual requirements (verification). Data validation, verification, and usability assessment will be conducted as outlined in this QAPP.

The data generated from the sampling program will be subjected to a multi-tiered review process described below. This process includes:

- A review of the data at the bench and field levels;
- A secondary review of field records by the Field Manager and analytical results within the laboratory by the lab QA/QC Manager to verify the data against method and SOP requirements;
- A review of the verified data by the Project Manager or designee for reasonableness and to identify obvious data anomalies;
- A validation by an objective third party, if necessary; and
- An assessment of the data by project team members for its usability to meet the project goals.

4.1 Data Review, Verification and Validation (D1)

All environmental measurement data collected by project staff will be subjected to quality control checks before being utilized in the interpretive reporting. A data generation system that incorporates reviews at several steps in the process is designed to protect the integrity of the data and reduce the number of data that do not meet the Data Quality Objectives (DQOs) or the project goals. This section describes the requirements of each review step that will be used in this project.

4.1.1 Data Verification Requirements

Data verification will occur at the field and laboratory level. This section describes the requirements of the data verification.

Field Activities Data Verification. The field personnel will be responsible for ensuring that the samples are collected and handled according to the specified procedures. Sample collection verification will include confirming that the samples were collected with the proper equipment at the appropriate locations with the appropriate frequency. Sample handling verification will include confirming that the samples were stored in the appropriate containers with the correct preservative, that the samples were stored at the proper temperature during transport from the field to the laboratory, and that all of the appropriate information is logged on the chain-of-custody records.

Lab Activities Data Verification. The laboratory will be responsible for verification of laboratory-generated data, although the laboratory SOPs for each method may require some components of the verification to also be conducted at the bench level. Laboratory verification will include assessing that

the procedures used to generate the data are consistent with the method requirements as specified in the laboratory's SOPs and that the QA/QC requirements for each method are met. Examples of method requirements include verifying the calibration and data reduction procedures. However, these requirements vary by analyte and are presented in more detail in the laboratory QA/QC Manual.

4.1.2 Data Review Requirements

The Field Manager will perform data reviews that consist of screening the field data sheets and laboratory data sheets according to established criteria listed in this section. If the established screening criteria are not met, an additional review of available laboratory data (e.g., quality control checks, relevant laboratory bench sheets) may be conducted. Investigation of the issue will be documented and the data will be discarded or flagged appropriately, identifying the limitations of the data.

Field Data Sheet Reviews. The following criteria may be used to screen the physical parameter measurements recorded by the field crews:

- temperature readings – check for reasonableness of values
- dissolved oxygen readings –compare concentrations to percent saturation

Laboratory Data Sheet Reviews. The following criteria will be used to screen the analytical measurements performed by the contract laboratory:

- field blanks (including equipment rinse blanks) –values should be less than detection limits
- laboratory method blanks –values should be less than detection limits
- review of all analytical results – check for reasonableness of values

4.1.3 Data Validation Requirements

Data validation is typically performed by someone independent of the project activity and not associated with the organization responsible for producing the dataset. However, the data validator needs to be familiar with both the data validation requirements and the project objectives. A scientist/engineer not directly involved in the project administration, project management, field or laboratory operations will conduct the data validation. There are four requirements in the data validation process as follows:

- Inspect the data verification and review records to ensure that no oversights were made during that process.
- Evaluate the data against the project DQOs. If data do not meet one or more of the DQOs, the data validation process will include an investigation into causes and an assessment of the impact of the noncompliant data on project objectives.
- Evaluate the data in the context of the project's overall objectives.
- Communicate the data validation results to the rest of the project team.

4.2 Verification and Validation Methods (D2)

All environmental measurement data and samples collected by project staff will be subjected to quality control prior to being entered into the project database. This is a multi-step process where the laboratory QA/QC Manager will have primary responsibility for verifying the data and a third party, preferably one who is not involved in data collection or analysis, conducts the data validation. These steps are described in more detail in the following sections.

4.2.1 Data Verification

This section describes the procedures that will be utilized in this project for verifying the data against method, procedural and/or contractual requirements.

Field Activities Data Verification. Individual crew leaders will verify the completion of their field data sheets and chain-of-custody forms. In addition, crew leaders will also verify the proper calibration and operation of their multi-parameter instruments. At the completion of each monitored event, the Field Manager will review all field data sheets, calibration sheets, and chain-of-custody forms for accuracy and completeness. The Field Manager will also verify that monitoring QA objectives for all accuracy, precision, completeness, and adherence to the required collection techniques are being met.

Laboratory Analytical Results Verification. Individual analysts will verify the completion of the appropriate analytical test and required bench sheets. The laboratory Technical Director or designee will review calculations and inspect laboratory bench sheets and log books daily to verify their accuracy, completeness, and adherence to the specified analytical method protocols. Calibration and QC data will be examined daily by the individual analyst. The laboratory Technical Director or designee will verify that all instrument systems are operating within control limits and that QA objectives for accuracy, precision, completeness, and adherence to the required detection limits are being met.

A summary of reportable QA/QC results and any non-conformance issues will be included in the laboratory deliverable to the Field or Project Manager.

4.2.2 Data Validation

This section describes the process that will be used to validate the data generated for this project. The first requirement is to inspect the data verification results and review records to ensure that no oversights were made during that process. A complete set of field and laboratory information will be provided to the data validator for this task.

The primary objective of the data validation in this project is to evaluate the data conformance with the project DQOs. These DQOs include criteria for accuracy, precision, completeness, and compliance with required detection limits. The components described under the Data Management Section of this QAPP will provide the necessary information to make this evaluation. The following must be reviewed as part of the measurement data and analytical data validation activities:

- field measurement data,
- field sample collection information,
- sample custody records,
- laboratory analytical results,
- data review information and/or laboratory case narrative,
- quality control data.

The data validator will be a LimnoTech environmental engineer or scientist, and will conduct a systematic review of the data for compliance with the established quality control criteria based on field duplicate, laboratory replicate, spiked sample media, spiked laboratory control samples, and blank data results provided by the laboratory. In addition, quality assurance evaluations of data accuracy, precision, and completeness will be performed on the field measurement data and the laboratory analytical results for each monitored event. The data validation qualifiers listed in Table 8 will be used when validating the data:

Table 8. Data Validation Qualifiers

Qualifier	Definition
U	The material was analyzed for, but was not detected above the level of the associated value. The associated value is either the sample quantitation limit or the sample detection limit.
J	The associated value is an estimated quantity.
R	The data are unusable (note: analyte may or may not be present)
UJ	The material was analyzed for, but was not detected. The associated value is an estimated level.

If quality control checks or objectives were not met, an investigation of the non-conformance may be initiated by the data validator with the project team personnel, such as the Field Manager, the laboratory QA/QC Manager, and the Project Manager. The non-conformance will be documented and the affected data set will be flagged appropriately, identifying any limitations.

Another objective of the data validation is to evaluate the data within the context of the project goals. These goals include providing datasets that can be used to develop model inputs, to calibrate and validate the models, and to ensure consistency among different sources of data. Suitable datasets for the modeling portion of this project will be based on the data quality assessment described above as well as an assessment of the spatial and temporal extent of the sample collection. Comparability with other sources of data will be evaluated by comparing and, if necessary, plotting the data with previously collected data to identify outliers or anomalous values.

The data validation results will be communicated to the project team in the form of a summary table that lists the validation tasks and the associated results and conclusions. If the validated dataset includes non-compliant data, this data will be addressed in a memo that accompanies the summary table. Data qualifiers assigned to the data during validation will be maintained in the project database to ensure communication of validation results with current and future data users.

4.3 Reconciliation with User Requirements (D3)

Once all field measurements and analytical data have been reviewed, quality control measures assessed, and any problems addressed, the measurement and analytical data will be assessed by the Project Manager or designee.

The assessment of the information generated from the monitoring program will be initiated by entering all analytical data and field measurement data into the project database. Other data (such as precipitation, flow data, velocity data, stage data, field notes, and information on any sampling anomalies) may be appended. All of these data will be evaluated and any relationships or correlations will be noted. The compilation of all information surrounding a sampling and/or monitoring event will be available to facilitate reconciliation with user requirements.

5 References

Illinois Environmental Protection Agency (IEPA). 2012. *Illinois Integrated Water Quality Report and Section 303(D) List, 2012.* Clean Water Act Sections 303(d), 305(b) and 314 Water Resource Assessment Information and List of Impaired Waters Volume I: Surface Water. Bureau of Water, Division of Water Pollution Control. Springfield, Illinois.

United States Environmental Protection Agency (EPA), 1998. *EPA Guidance for Quality Assurance Project Plans*, EPA QA/G-5. Washington, DC.

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Appendix A
Standard Operating Procedures for Field Activities

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I. Introduction

This standard operating procedure (SOP) is applicable to the collection of representative liquid samples, both aqueous and non-aqueous, from streams, rivers, lakes, ponds, lagoons, and surface impoundments. It includes samples collected from depth, as well as samples collected from the surface. These typically applicable procedures have been adapted from the U.S. EPA Environmental Response Team Surface Water Sampling SOP No. 2013, dated 11/17/94 and may be varied or changed as required, dependent upon site conditions or equipment and procedural limitations. The actual procedures used should be documented in the field notes, especially if changes are made.

There are two primary interferences or potential problems with representative surface water sampling. These include cross contamination of samples and improper sample collection. Following proper decontamination procedures and minimizing disturbance of the sample site will eliminate these problems as follows:

- Cross contamination problems can be eliminated or minimized through the use of dedicated sampling equipment. If this is not possible or practical, then decontamination of sampling equipment is necessary. Refer to the Equipment Cleaning SOP.
- Improper sample collection can involve using contaminated equipment, disturbance of the stream or impoundment substrate, and sampling in an obviously disturbed area.

In order to collect a representative sample, the hydrology and morphometry of a stream or impoundment should be determined prior to sampling. This will aid in determining the presence of phases or layers in lagoons or impoundments, flow patterns in streams, and appropriate sampling locations and depths. In addition, water quality indicator data may be collected, if necessary, in impoundments to determine if stratification is present. Measurements such as dissolved oxygen, pH, temperature, and redox potential can indicate if strata exist which would affect analytical results. Measurements should be collected at sufficiently sized intervals (e.g., 1 meter) from the substrate to the surface using the appropriate instrument (e.g., Hydrolab).

II. Materials

The following materials shall be available, as required, during surface water sampling. Back-up field instruments/equipment should be available, if required.

- Personal protective equipment (as necessary);
- Cleaning equipment (as required in the Standard Operating Procedure for Equipment Cleaning);
- Appropriate sampling apparatus and accessories (e.g., Kemmerer, weighted bottle, or Dip sampler, sample containers, sampling line, weights, messengers);
- Appropriate sample bottles, preservatives (if required) and sample bottle labels;
- Ziploc^{R}-type bags;
- Insulated coolers, ice, and appropriate packing material;
- Chain of Custody records and custody seals;

- Field data sheets, field log book, waterproof pen, camera and film;
- Decontamination equipment;
- Maps/plot plan, survey stakes/flags/buoys and anchors;

III. Preparations

- Determine the extent of the sampling effort, the sampling methods to be employed, and the types and amounts of equipment and supplies needed.
- Obtain the necessary sampling and monitoring equipment to suit the task. Consider sample volume, depth, deployment circumstances (shore, wading, boat, currents), type of sample, sampler composition materials, and analyses to be conducted.
- Decontaminate or pre-clean equipment and ensure that it is in working order.
- Prepare scheduling and coordinate with staff, clients, and regulatory agency, if appropriate.
- Perform a general site survey.
- Use stakes, flagging, or buoys to identify and mark all sampling locations. If required, the proposed locations may be adjusted based on site access, property boundaries, and surface obstructions. If also collecting sediment samples, this procedure may disturb the bottom and cause interferences with collection of representative water samples.

IV. General Sample Collection Procedures

1. Record pertinent data on the field log (see attached Surface Water Sampling Field Log, or equivalent).
2. Label all sample containers with the date, time, site location, sampling personnel, and other requested information.
3. Don appropriate personal protective equipment (as necessary).
4. For fecal coliform bacteria samples, use a sterile sample bottle and store the bottle cap in a sterile plastic bag to prevent contamination during sampling.
5. Clean all sampling equipment prior to sample collection according to the procedures in the Standard Operating Procedure for Equipment Cleaning.
6. At designated surface water sampling locations, thoroughly rinse the sampler in the water body prior to collecting the first sample.
7. For samples requiring field filtering, use a pump and in-line disposable filter, if possible to collect the sample directly into the sample container.
8. If field preservation is required, place appropriate preservative into the sample container prior to sample collection. Note the preservative and preservative column on the sample container and sampling log.
9. If any quality control samples are specified, they will be collected in the following manner:

- Duplicate samples should be collected at the same time or immediately following one another in accordance with the above procedures. If blind duplicate samples are specified, one of the duplicate samples should be labeled so that it does not identify

the other sample of the duplicate pair to the laboratory on the chain-of-custody (COC). For example, one sample of the duplicate pair would be labeled following the normal protocol, while the second would be labeled with a sample ID of "DUPLICATE" and a blank line placed in the location, date and time boxes of the sample label. It is important that the duplicate pair samples are identified separately in the field notes with information including location, sample ID (as entered on the sample container label and COC), sample date and time so that analytical results can be paired after received from the laboratory.

- Rinse (or equipment) blanks should be collected from a final distilled/deionized water rinse of the specified sampling equipment after that piece of equipment has been cleaned in accordance with appropriate specified cleaning procedures.
- Field blanks, such as samples of water or reagents used to clean sampling equipment, should be collected directly into the sample bottle from the appropriate source container.

10. Record sample collection information on the field log and store the samples in an iced cooler as described in the Standard Operating Procedure for the Shipping and Handling of Samples.
11. Handle, pack, and ship samples according to the procedures in Standard Operating Procedure for the Shipping and Handling of Samples.

V. Equipment-Specific Sample Collection Procedures

Kemmerer Bottle. A Kemmerer bottle may be used in most situations where site access is from a boat or structure such as a bridge or pier, and where samples at depth are required. Sampling procedures are as follows:

1. Use a properly cleaned Kemmerer bottle. Set the sampling device so that the sampling end pieces (upper and lower stoppers) are pulled away from the sampling tube (body), allowing the substance to be sampled to pass through this tube.
2. Lower the pre-set sampling device to the pre-determined depth. Avoid bottom disturbance.
3. When the Kemmerer bottle is at the required depth, send down the messenger, closing the sampling device.
4. Retrieve the sampler and discharge from the bottom drain the first 10-20 mL to clear any potential contamination of the valve.
5. Transfer the sample to the appropriate sample container, as necessary, and cap securely.

Weighted Bottle Sampler. A weighted bottle sampler may be used in situations similar to those outlined for the Kemmerer bottle, but for near surface samples. Sampling procedures are as follows:

1. Use a thoroughly cleaned weighted bottle sampler with clean and/or disposable sample containers. For fecal coliform bacteria samples, use a sterile sample bottle

with the special sample bottle holder and store the bottle cap in a sterile plastic bag to prevent contamination.

3. Upon arrival at each field site, thoroughly rinse the sampler in the stream prior to collecting the first sample.
4. At the designated sampling location, carefully lower the weighted bottle sampler, allowing the sampler to fully submerse and fill with water. Fecal coliform samples will be collected just below the surface of the stream at the center of flow.
5. Retrieve the sampler, transfer the sample to the appropriate sample container, as necessary, and cap securely.

Dip Sampler

A dip sampler is useful in situations where a sample is to be recovered from locations (e.g., outfall pipe, sump manhole, along a pond or lagoon bank) where direct access is limited. The long handle (or line if sampling from a bridge or other structure directly above the water body) on such a device allows access from a safe location. Sampling procedures are as follows:

1. Assemble the device in accordance with the manufacturer's instructions.
2. Thoroughly clean the sampler prior to use and use only clean sample containers.
3. Upon arrival at each field site, thoroughly rinse the sampler in the stream prior to collecting the first sample.
4. Extend the device to the sample location and fill the sample container by dipping and/or submersion.
5. Retrieve the sampler, transfer the sample to the appropriate sample container, as necessary, and cap securely.

Direct Method

For streams, rivers, lakes, and other surface waters, the direct method may be used to collect water samples from the surface directly into the sample bottle. This method may not be appropriate for sampling lagoons or other impoundments where contact with contaminants is a concern. When using the direct method, do not use pre-preserved sample bottles as the collection method may dilute the concentration of preservative necessary for proper sample preservation. The procedures are as follows:

1. Using adequate protective clothing, access the sampling station by appropriate means.
2. For shallow stream stations, collect the sample under the water surface while pointing the sample container upstream. The container must be upstream of the collector. Avoid disturbing the substrate.
3. For lakes and other impoundments, collect the sample under the water surface avoiding surface debris and boat wakes.

VI. Disposal Methods

If required, all water generated during equipment cleaning procedures will be collected and contained on site for determination of proper treatment or disposal. In addition, personal protective equipment (e.g., gloves, disposable clothing) and other disposable equipment resulting from cleaning and sampling procedures will be placed in plastic bags and appropriately contained for proper disposal.

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SURFACE WATER SAMPLING FIELD LOG

Project Name: Project Code: Page __ of __

Date	Time	Sample ID	Sample Location	Equipment Used	Samplers	Comments

Notes:

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I. Introduction

This standard operating procedure (SOP) is applicable to the collection of representative data (stream dimensions and water velocity) for use in determining discharge in streams and open channels. These typically applicable procedures have been adapted from the USGS *Techniques in Water Resources Investigations*, Book 3, Chapter A8: Discharge Measurements at Gaging Stations (http://water.usgs.gov/pubs/twri/twri3a8/pdf/TWRI_3-A8.pdf) and the *Open Channel Profiling Handbook*, January 1989 (Rev. May 1, 1990), Marsh-McBirney, Inc. The procedures herein may be varied or changed as required, dependent upon site conditions or equipment and procedural limitations. The actual procedures used should be employed in consultation of the more detailed procedures found in the USGS discharge measurement guidance document and the actual procedures used should be documented in the field notes, especially any changes made.

II. Materials

The following materials shall be available, as required, during collection of surface water flow data. Back-up field instruments/equipment should be available, if required.

- Personal protective equipment (as necessary);
- Boat and/or waders;
- Cleaning equipment (see the Standard Operating Procedure for Equipment Cleaning);
- Flowmeter/velocimeter and appropriate accessories (e.g., Marsh-McBirney Flo-Mate 2000, Pigmy-Gurly velocimeter, profiling/wading rod, boat/bridge board with suspension cable and weight, operation manuals);
- Protractor and compass;
- Measuring tape and/or measuring wheel;
- Field data sheets, field log book, waterproof pen, camera and film;
- Maps/plot plan, survey stakes/flags/buoys and anchors;

III. Preparations

- Determine the extent of the sampling effort, the methods to be employed, and the types and amounts of equipment and supplies needed.
- Obtain the necessary sampling and monitoring equipment to suit the task. Consider stream morphometry (width, depths, channels) and deployment circumstances (bridges, shoreline, wading, boats, obstructions, currents).
- Decontaminate or pre-clean equipment and ensure that it is in working order.
- Prepare scheduling and coordinate with staff, clients, and regulatory agency, if appropriate.
- Perform a general site survey.
- Use stakes, flagging, or buoys to identify and mark all sampling locations. If required, the proposed locations may be adjusted based on site access, property boundaries, and surface obstructions.

IV. Flow Measurement Procedures

The methods of determining cross-sectional area and velocity must be selected prior to the field event. Data required for use in calculation of stream flow includes measurements of cross-sectional area (water depth and transect segment width), water velocity, flow angle, and transect angle. The mid-section method of computing cross-sectional area for discharge measurements is recommended by USGS and there are a number of different methods for measuring velocity. The two methods of velocity measurement that follow are frequently used for normal stream conditions:

- Six tenths Depth Method (0.6 depth below the water surface) uses observed velocity at this depth as the mean velocity in the vertical. This method gives extremely reliable results whenever the water depth is between 0.3 and 2.5 feet. It is also quicker to measure so is good for times of rapidly changing water level (stage).
- Two Point Method (0.2 and 0.8 depth below the water surface) averages velocities observed at these relative depths at each location and this average is used as the same mean velocity in the vertical. This method gives more consistent and accurate results than any of the other methods except the vertical-velocity curve method. The two point method is generally not used at depths less than 2.5 feet because the current meter settings would be too close to the water surface and stream bed for dependable results.

Flow measurement data collection using wading techniques are preferred by USGS, if conditions permit. Wading measurements offer the advantage over measurements from bridges (or other techniques such as cableways, not discussed herein) in that it is usually possible to select the best of several available cross-sections for the measurement.

When a stream cannot be waded, bridges may be used to obtain flow measurements (though cableway measurements are usually better, if available). No set rule can be given for choosing between the upstream or downstream side of the bridge to collect flow data. The advantages of using the upstream side of the bridge are:

- Hydraulic characteristics at the upstream side of bridge openings usually are more favorable.
- Approaching drift can be seen and be more easily avoided.
- The streambed at the upstream side of the bridge is not likely to scour as badly as at the downstream side.

The advantages of using the downstream side of the bridge are:

- Vertical angles are more easily measured because the sounding line will move away from the bridge.
- The flow lines of the stream may be straightened out by passing through a bridge opening with piers (see points under step 2 below).

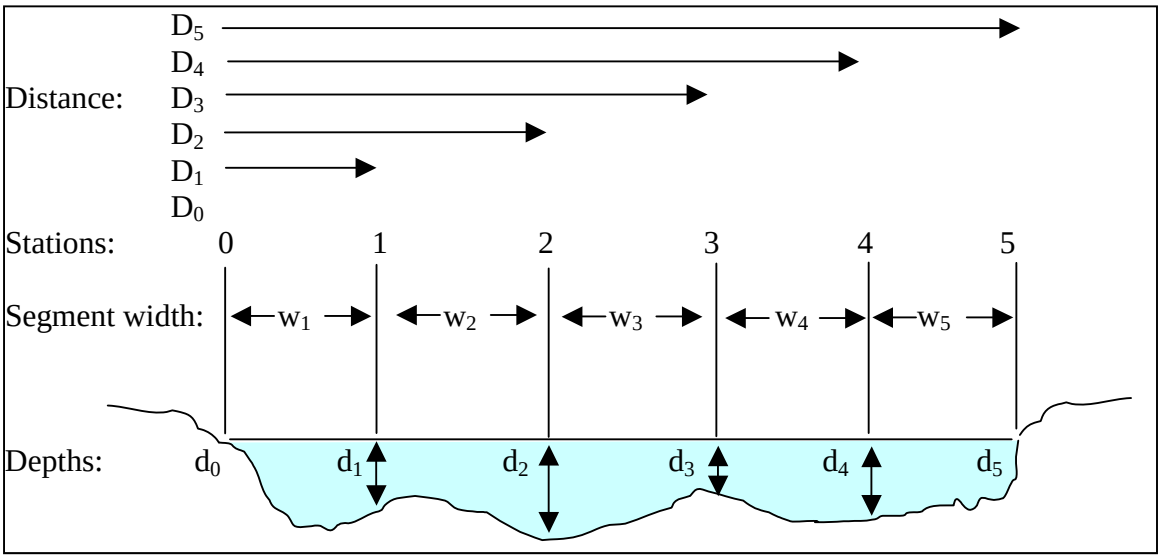
To accomplish flow data collection using the methods selected, a transect of measurement stations across a stream is set up and marked before collecting section depth, width, and velocity data using the following steps:

1. Follow appropriate safety procedures and use personal protective equipment as necessary.
2. Select the transect site location following as many of the following considerations as possible:
   - The channel should have as much straight run as possible – at least such that the length upstream from the profile should be twice the downstream length.
   - The channel should be free of flow disturbances. Look for protruding pipe joints, sudden changes in diameter, contributing sidestreams, outgoing sidestreams, or obstructions.
   - The flow should be free of swirls, eddies, vortices, backward flow, or dead zones.
   - Avoid areas immediately downstream from sharp bends or obstructions.
   - Avoid converging or diverging flow (approach to a flume) and vertical drops.

- Avoid areas immediately downstream from a sluice gate or where the channel empties into a body of stationary water.

3. Determine the width of the stream starting and ending at the stream's edges. Use a measuring wheel on a bridge or string a measuring tape between stakes if wading or in a boat.
4. Record the angle of the transect with respect to the stream channel and direction of flow. The transect should most preferably be at right angles to the direction of flow to avoid having to correct for the angle of the transect when calculating discharge.
5. Mark/record the partial section locations (measurement recording stations) of the measurement transect. These should be spaced so that no partial section contains more than 10 percent of the total flow. The ideal measurement would have less than 5 percent of the flow in any one partial section. Equal width partial sections across the transect are not recommended. Make the width of the partial sections less as depths and velocities become greater.
6. Assemble the appropriate equipment for the velocity and depth measurements.
7. Prepare the measurement note sheets to include the following information:
   - Name of stream and exact location of transect site.
   - Date, party, type of meter suspension, type of meter.
   - Measurement data (depth, width, position location, velocity, flow angle, time measurements were started and ended).
   - Bank of stream that was the starting point. Identify the stream bank by either LEW or REW (left edge of water or right edge of water, respectively) when facing downstream.
   - Gage height measurement and corresponding times.
   - Other pertinent information regarding site conditions and accuracy of the measurement.

8. Begin recording depth, width (transect distance) and velocity measurements at each station of the transect, successively, according to the remaining steps below and in reference to the figure that follows.



w = width of segment

D = distance from stream's edge

d = depth of water

9. Record distance (D1, D2, D3 …) from steam's edge at initial station (measurement point 0) to each successive station (1, 2, 3, …).
10. Record the water depth (d0, d1, d2, d3, …) at each measurement point, including the edge of the water at each end of the transect.
11. Measure velocity (0.2 depth & 0.8 depth – or – 0.6 depth below water surface) at each station and record the reading and associated meter depth position (0.2, 0.6, 0.8). Follow manufacturer instructions for operation of the meter.

    Note: If wading, stand in a position that least affects the velocity of the water passing the meter sensor (sufficiently downstream or to the side of the sensor – approximately an arm's length). Avoid standing in the water if feet and legs would occupy a considerable percentage of the cross section of a narrow stream (use a plank or other support). Keep the wading rod in a vertical position and the velocity sensor parallel to the direction of flow.
12. Measure and record the angle of flow with respect to the transect and direction of flow, especially if the flow is not at right angles to the transect.

V. Discharge Calculation

The USGS-preferred midpoint method of determining discharge uses the products of the partial areas of the stream cross-section (segment) and their respective average velocities (Q = A * V). It is assumed that the velocity measurement at each station represents the mean velocity in a partial rectangular area. The area extends laterally from half the distance from the preceding station to half the distance to the next and vertically from the water surface to the sounded depth. The cross-section is defined by depths at the station locations (d_1, d_2, …, d_n). There are two cases in the calculation, as follows:

For segments in the middle of the transect:

$$Q_{middle\text{-}segment} = (D_{n+1} - D_{n-1})/2 * d_n * V_n$$

For segments at the end of the transect:

$$Q_{first\text{-}end\text{-}segment} = (D_{n+1} - D_n)/2 * d_n * V_n$$
$$Q_{last\text{-}end\text{-}segment} = (D_n - D_{n-1})/2 * d_n * V_n$$

- $Q = A * V$ (discharge = area * velocity; where)
- $A = w * d$ (area = width * depth; where)
- $w = D_{n-1} - D_{n+1}$ or $D_{n+1} - D_n$ or $D_n - D_{n-1}$
  (segment width = distance between alternate or adjacent stations; and)

Sum the segment discharges to get the total discharge for the river at a particular location

VI. Other considerations for less than ideal site conditions:

Non-perpendicularity:

Ideally, the cross-section is perpendicular to the stream channel, which has a straight run of sufficient length, and the stream flow is perpendicular to the cross-section. However, this is not always possible in the real world.

Angle of flow measurements should be collected and incorporated into the discharge calculation when flow is not perpendicular to the stream cross-section (insufficient straight run length of channel, presence of swirls, eddies, etc.).

Calculation of discharge should consider only the velocity component vector that is parallel to the stream channel (perpendicular to the ideal cross-section). This can be obtained by multiplying the velocity reading by the cosine of the flow angle (V * cos(a)). If the cross-section measurements are taken from a bridge that is not perpendicular to the stream channel, then correction for the angle of the bridge is also necessary.

Backwater and reverse flow:

Backwater areas or areas to shallow to measure are usually assigned a velocity of zero. Velocity values in areas of flow reversal (from eddies, or lake seiche effects near river mouths) must be assigned the opposite sign (if downstream velocities are positive, upstream velocities are negative).

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Flow Monitoring Datasheet

Site: _____

Crew: _____ Date: _____

Staff Gage Reading (ft): _____ Begin Time: _____

Tape Down (ft): _____ End Time: _____

Equipment Used:

Transect Starting Point is on (circle one): left bank facing downstream right bank facing downstream

Bridge measurements are from (circle one): upstream side downstream side

Distance Starting Point to Nearest Edge of Water (ft): _____

Distance Ending Point to Nearest Edge of Water (ft): _____

Depth at Left Edge of Water (facing downstream): _____

Depth at Right Edge of Water (facing downstream): _____

Observations:

Transect Point No.	Transect Tape Reading (ft)	Water Depth (ft)	0.8D Velocity (ft/s) (if Depth >2.5 ft)	0.2D Velocity (ft/s) (if Depth >2.5 ft)	0.6D Velocity (ft/s) (if Depth <2.5 ft)	Angle coeff.	Notes

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I. Introduction

The equipment cleaning procedures described in this document include pre-field, in-field, and post-field cleaning of sampling equipment. The sampling equipment may consist of surface water sampling devices; water testing instruments; or other activity-specific sampling equipment. All non-disposable sampling equipment will be cleaned after completion of each sampling event. If appropriate, cleaning procedures will be monitored through the analysis of rinse blank samples as described in the project QAPP. Equipment cleaning areas will be located within or adjacent to a specific work area as necessary.

II. Materials

The following materials will be available during equipment cleaning, as needed:

- Personal protection equipment (as necessary);
- Distilled/deionized water;
- Non-phosphate detergent (Alconox, Liquinox, or equivalent);
- Tap water;
- Appropriate cleaning solvent (e.g., methanol, nitric acid);
- High-pressure hot water/steam cleaning unit;
- Wash basins;
- Brushes;
- Polyethylene sheeting;
- Aluminum foil;
- Plastic overpack drum, garbage can, or stainless steel tubes (for bladder or other pumps);
- Large heavy-duty garbage bags;
- Spray bottles (to hold tap water, distilled/deionized water, methanol, or nitric acid); and
- Disposable and/or heavy duty reusable (PVC, latex or nitrile) gloves.

III. Storage of Equipment

All cleaned sampling equipment will be stored in a clean environment and, if appropriate, the equipment will be covered/sealed with aluminum foil.

IV. Safety Procedures During Equipment Cleaning

1. Personnel will wear the following personal protection equipment as necessary, when cleaning sampling equipment (e.g., Kemmerer sampler, split-spoon sampler, trowels) and larger equipment (e.g., drill rig, augers):

    - Safety glasses, goggles, or a splash shield; and
    - PVC, latex, or nitrile outer gloves,
    - Coated Tyvek® disposable coveralls or rainsuit, optional for small equipment cleaning; and
    - Chemical resistant over boots, optional for small equipment cleaning.

2. All solvent rinsing if required, will be conducted in an adequately ventilated area.

3. All solvents transported into the field will be stored and packaged in appropriate containers with care taken to avoid exposure to extreme heat.

4. Handling of solvents will be consistent with the manufacturer's Material Safety Data Sheets (MSDS).

V. Field Cleaning Procedures

Cleaning Station

If a designated field equipment cleaning station location is required, it will be established to conduct all cleaning at each work area of the Site. The field equipment cleaning station will be located away from the immediate work area to minimize adverse impacts from work activities on the cleaning procedures, but close enough so the sampling teams can minimize equipment handling and transport.

Cleaning of Smaller Sampling Equipment

Cleaning of smaller sampling equipment (e.g., Kemmerer samplers, sample composite vessels, split-spoon samplers, bailers, trowels) will be conducted according to the following sequential procedure:

- Non-phosphate detergent (Alconox, Liquinox, or equivalent) and tap water wash;
- Tap water rinse;
- Solvent rinse, if required (e.g., methanol for organic constituent analysis, nitric acid for inorganic constituent analysis); and
- Triple distilled/deionized water rinse.

The first step, non-phosphate detergent and tap water scrub, is intended to remove all visible particulate matter and residual oil and grease. This may be preceded by a steam cleaning to facilitate soils removal. The tap water rinse is necessary to remove all soapy residues. The need for a specific solvent used for the solvent rinse, if required in the QAPP, will depend upon what the sample will be analyzed for. The final rinse of distilled/deionized water will be repeated three times. The equipment will then be allowed to air dry.

Collection and Disposal of used Solvents, Residuals and Rinse Solutions

All solvents, residuals, and rinse waters generated during the cleaning of equipment on-site will be collected, containerized, and stored on-site until arrangements can be made for proper disposal.

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I. Introduction

This standard operating procedure (SOP) is applicable to the collection of representative sediment oxygen demand (SOD) data from streams, rivers, lakes, ponds, lagoons, and surface impoundments. These typically applicable procedures have been adapted from the Ohio EPA Sediment Sampling Guide and Methodologies (OEPA, 2001), and may be varied or changed as required, dependent upon site conditions or equipment and procedural limitations. The actual procedures used should be documented in the field notes, especially if changes are made.

In order to collect representative SOD data, the hydrology and morphometry of a stream or impoundment should be determined prior to sampling. This will aid in determining appropriate sampling locations (see Section II).

SOD is measured using a dark chamber (resembling a large, inverted bowl) that isolates a known area of sediment and a known volume of water. A pump and tubing are used to form a closed system loop to circulate the volume of water over the area of sediment and ensure complete mixing. A dissolved oxygen (DO) probe in the chamber provides a continuous display of the DO concentration inside the chamber, which is recorded every five minutes for two hours or until the DO drops by 2 mg/L.

By using a dark chamber, photosynthesis does not affect the DO of the water in the chamber, and respiration and SOD are the only influences in the DO chamber. The effects of respiration are quantified by filling a blank SOD chamber or dark bottle with a known volume of water from the same location as the measurement chamber and measuring the DO at the beginning and end of the SOD test. The change in DO in the blank chamber or dark bottle provides an estimate of the amount of DO consumed by algal respiration in the water column.

The rate of change of DO in the chamber is determined by plotting the DO recorded in the chamber every five minutes. A regression analysis is then performed on the dataset. The rate of change of DO in the chamber is equal to the slope of the regression. The respiration rate measured in the dark bottle is subtracted from this rate. The corrected value is then divided by the area of the underlying sediment, resulting in an SOD value expressed as grams of oxygen consumed per square meter per day (g/m2/day) at the ambient temperature. To provide for standardization, temperatures are usually corrected to 20 degrees Celsius using a temperature correction factor.

II. Site Selection

SOD should be evaluated when any of the following conditions exist:

- Reaches having extensive low velocity pools (less than 0.25 fps).
- Reaches having diurnal DO swings greater than 100%.
- Reaches having extensive sludge deposits.

Sites should be selected based on a field evaluation that includes:

- Stream velocity; less than 0.25 fps (Velz, 1970), i.e., pools.
- Discharger location.
- Accessibility.
- Presence and extent of sludge deposits. Sludge deposits present the greatest impact of sediment types on instream DO. Sites for SOD measurement should include sludge deposits, if present, or locations with hydraulic characteristics conducive to sludge deposition.

III. Materials

The following materials shall be available, as required, during SOD surveys. Back-up field instruments/equipment should be available, if required.

- Personal protective equipment (as necessary).
- Cleaning equipment (as required in the Standard Operating Procedure for Equipment Cleaning).
- SOD chambers (benthic respirometer) and accessories (mixing pump with tubing and fittings, battery with connecting cables, rheostat for adjusting pump velocity).
- DO Meters – YSI Model 56 DO meter for each chamber, YSI Model 57 DO meter for algal production outside chamber, chart recorder.
- Primary productivity bottles, rope.
- Turbidimeter and accessories.
- Pyranograph and photometer with submersible sensor.
- Sediment sampling equipment (scoop, ponar dredge, etc.).
- Field data sheets, field log book, waterproof pen, camera and film.
- Miscellaneous supplies: Maps/plot plan, extra rope, bungee cords, survey stakes/flags/buoys, anchors and safety equipment.

IV. Preparations

- Determine the extent of the sampling effort, the sampling methods to be employed, and the types and amounts of equipment and supplies needed.
- Decontaminate or pre-clean equipment and ensure that it is in working order.
- Prepare scheduling and coordinate with staff, clients, and regulatory agency, if appropriate.
- Perform a general site survey.
- Use stakes, flagging, or buoys to identify and mark all sampling locations. If required, the proposed locations may be adjusted based on site access, property boundaries, and surface obstructions. If also collecting sediment samples, this procedure may disturb the bottom and cause interferences with collection of representative water samples.

V. SOD Instrument Setup and Measurement Procedures

Benthic Respirometer – Instrument Setup

1. Measure and record on SOD data sheet: water velocity at 0.2 feet above sediments, SOD chamber number.

2. Calibrate DO meter. Record DO concentration near water surface.

3. Place chamber in sediments. If sediments are disturbed, wait several minutes before proceeding.

4. Purge all air from the mixing pump and tubing by running the pump for a sufficient time period with tubing ends under water.

5. Attach the mixing pump inlet and outlet tubing to the SOD chamber fittings. Turn on pump to begin mixing water and verify that no air is trapped within chamber.

6. Insert the DO probe in the chamber. Verify that no air bubbles are introduced inside the chamber via the probe.

7. If possible, regulate water velocity within chamber to approximate stream velocity near the sediments outside the chamber. If a rheostat is used in-line with the pump, the rheostat settings will need to be calibrated to velocity using the pump and tubing, a bucket and a flowmeter.

8. Install a similar respirometer next to the first one, but seal the bottom with a plastic lid, excluding all sediment (for quality control "blank" measurements). This chamber will measure the respiration oxygen demand of the water column, to be subtracted from the DO change measured by the first SOD chamber. If only one chamber is available, use the DO change measured in the dark productivity bottles to make this correction.

9. Start the DO meter.

10. Record the starting time, date, site data, meter number and, if using a non-auto-recording DO meter, manually record the DO and temperature readings on the SOD field data sheet. Write the values at 5 minute intervals initially, and alter the interval depending on the rate of oxygen uptake.

11. Retrieve chamber after DO concentration has decreased by 2 mg/l or after two hours.

VI. Calculations

The following equation is used to determine the SOD:

SOD = 1.44 * (V/A)*(b1-b2) where:

SOD	=	sediment oxygen demand, in g/m2/day
1.44	=	conversion factor, converts results to g/m2/day
V	=	volume of chamber, in liters

A = area of chamber, in square meters (A=p*r2)
b1 = rate of change of DO inside the SOD chamber, in mg/L/minute
b2 = rate of change of DO inside the "blank" SOD chamber or dark productivity bottles, in mg/L/minute

To facilitate the comparison of results among different sites, the SOD should be converted to 20^{o}C by using the following equation:

SOD20 = SODT/(1.065T-20) where:

SODT = SOD at original temperature, in g/m2/day
SOD20 = SOD at 20^{o}C, in g/m2/day
T = Ambient temperature, in ^{o}C

VII Disposal Methods

If required, all water generated during equipment cleaning procedures will be collected and contained for determination of proper treatment or disposal. In addition, personal protective equipment (e.g., gloves, disposable clothing) and other disposable equipment resulting from cleaning and sampling procedures will be placed in plastic bags and appropriately contained for proper disposal.

VIII. References

Ohio EPA. 2001. Sediment Sampling Guide and Methodologies, 2nd Edition. Division of Surface Water, Columbus, Ohio. Nov. 2001

Velz, Clarence. 1970. Applied Stream Sanitation. Wiley Interscience. New York, NY.

I. Introduction

Water quality parameters, such as water temperature, dissolved oxygen and pH are routinely measured during surface water investigations. Instantaneous measurements may be recorded using individual probes or multi-sensor sondes, as available and appropriate for each situation. These probes should be calibrated daily using manufacturer procedures. Collection of continuous data is most commonly performed using a data sonde with internal batteries and memory capacity that can be deployed for extended periods to record data over a range of conditions. The primary limiting factor for extended deployment duration is usually degradation of data quality because of biofouling of the sensor surfaces. The rate of biofouling is related to productivity of the water where monitoring is being conducted. In general, a sonde should be downloaded, checked for reading stability (drift), and recalibrated at a frequency of no more than seven to ten days. An initial check within this time period may allow for modification of subsequent visits, depending on the magnitude of drift observed. The calibration and maintenance log for the above referenced meters is included as an attachment to this Standard Operating Procedure.

II. Materials

The following materials, as required, shall be available for installation of and field visits to the continuous monitoring station(s):

- Personal protective equipment (as necessary);
- Perforated PVC housing(s) for extended deployment installations;
- Fence post(s) and pounder for extended deployment installations;
- Attachment hardware for extended deployment installations;
- Data probes or sonde;
- Manufacturer's operating manuals for each instrument;
- Calibration solutions appropriate for each instrument;
- Tools and equipment necessary for field maintenance of instruments;
- Laptop computer for setup and downloading sondes (as necessary);
- Clean container;
- pH calibration buffer solution within and bracketing expected range of measurements;
- Cleaning equipment (as required in the Standard Operating Procedure for Equipment Cleaning);
- Distilled/deionized water; and
- Appropriate forms and field notebook.

III. Procedures for Instantaneous Field Water Quality Measurements

1. Calibrate and operate all meters in accordance with manufacturer’s operating manuals.
2. For in-situ surface water measurements place probe(s) at the designated location in the water body, allow instrument readings to stabilize, and record the readings for each parameter:
3. If measuring ex-situ samples, collect a water sample from the designated location in the designated container, insert probes into container and record readings (especially temperature and pH readings) as soon as possible after collecting the sample to minimize inaccuracies from the changing temperature of the sample as it equilibrates to ambient temperature.
4. Rinse probes off in distilled/deionized water, if required.

5. Log results and observations in field notebook.

IV. Procedures for Extended Sonde Deployment and Continuous Measurements

Installation. Installation of the data sonde is accomplished using a perforated PVC housing attached to a fence post or other structure, if present and appropriate. The goal of the installation is to place the sensors in a location that is representative of the water column (e.g. mid-channel, mid-depth, middle of flow volume). It is important to consider water level fluctuations, obstructions, and debris that may be present during wet or dry weather conditions and plan the installation accordingly to maximize the collection of accurate data. After an appropriate location is identified, install the perforated PVC housing in the stream channel.

Data Sonde Set-up and Calibration. The dissolved oxygen and pH sensors are calibrated according to manufacturer specifications prior to installation. Temperature is usually a factory-calibrated parameter. A logging file is created in the sonde for the storage of data according to manufacturer specifications. Start date and time is specified to ensure that data logging occurs when the sonde is deployed. Specify the sampling interval/data recording frequency. After calibration and logging file set-up, remove calibration chamber and attach the weighted strainer. Place the sonde into the protective housing. Secure the cap to the housing. Record deployment time in field notes.

Field Maintenance. The data sonde should be maintained at a minimum frequency of every seven to ten days. The current readings should be checked to evaluate drift, the logging file should be downloaded, the sonde should be cleaned and recalibrated, and the sonde should be redeployed. Each of these activities is described below.

The readings being reported by the sensors are checked for drift by comparing to known values. Dissolved oxygen is compared to a winkler titration and pH readings are compared to calibration solutions. The procedure is as follows:

1. Collect a water sample using a 5-gallon bucket, taking care to minimize turbulence. Keep sample out of direct sunlight.
2. Remove sonde from housing, connect to laptop, and place sensors in sample bucket. NOTE: take care to minimize disturbance to sensors;
3. Record current dissolved oxygen reading;
4. Conduct a Winkler titration to determine dissolved oxygen concentration of sample. Perform this step with an aliquot of the water collected in step 1 and as near as possible to the same time the sonde DO reading is recorded. Treat both sample aliquots identically otherwise, collect;
5. Calculate relative percent difference (RPD) between Winkler and sonde dissolved oxygen readings using the formula noted below. The acceptance criterion for this comparison is an RPD of 20% or less.

$$RPD = \left| \frac{(Abs(Winkler\ D.O. - Sonde\ D.O.))}{(Winkler\ D.O. + Sonde\ D.O\ /\ 2)} \right| * 100$$

6. Record result in the field notebook;
7. Repeat process for the pH sensors;
8. Download logging file to laptop;
9. Gently clean the sensors to remove biofilms according to manufacturer specifications;
10. Recalibrate sensors;
11. Set up logging file;
12. Redeploy sonde, record date and time in field notes.

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FIELD INSTRUMENT CALIBRATION AND MAINTENANCE LOG
Temperature, pH and Dissolved Oxygen Meters

Instrument	Temperature	pH	D.O.
Manufacturer			
Model			
Identification No.			

Date	Time	Initials	Temp	pH			D.O.	Battery	Comments
			°C	4	7	10		Check	

.

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I. Handling

1. Fill in sample label (see attachment). Use indelible waterproof marking pen and include:
   - ♦ Sample Identification code (if possible, should reflect site name, sample location and sample interval)
   - ♦ Sample type (e.g., soil, sediment, water, vapor);
   - ♦ Project code;
   - ♦ Analysis required;
   - ♦ Date sampled;
   - ♦ Time sampled;
   - ♦ Name or initials of person who collected the sample;
   - ♦ Mode of collection (composite or grab); and
   - ♦ Preservation added, if applicable.
2. Check the caps on the sample containers so that they are tightly sealed.
3. Cover the label and sample container cap with clear packing tape to secure the label and cap onto the container, if necessary.
4. Place a signed custody seal label (see attachment) over the cap such that the cap cannot be removed without breaking the custody seal, if required.

II. Packing

1. If using a laboratory-supplied transpack, follow the laboratory's instructions for packing. Generally, repack the transpack in the same way in which the empty containers were received. If using a standard cooler, follow the instructions below.
2. Using packaging tape, secure the outside and inside the drain plug at the bottom of the cooler that is used for sample transport.
3. Place 1 to 2 inches of vermiculite or other cushioning material at the bottom of the cooler.
4. Place the sealed container upright in the cooler.
5. Place additional cushioning material around the sides of each sample container.
6. Place frozen gel cold packs on top of sample containers. If ice is used, repackage ice in small Ziploc® - type plastic bags and place loosely in the cooler. Do not pack cold packs or ice so tightly that it may prevent the addition of sufficient cushioning material.
7. Fill the remaining space in the cooler with vermiculite or other cushioning material.
8. Place the chain-of-custody forms (see attachment) in a large Ziploc® type bag and tape the forms to the inside of the cooler lid.

9. Close the cooler lid and fasten with packaging tape.
10. Wrap strapping or packaging tape around both ends of the cooler at least twice.
11. Mark the cooler on the outside with the following information: return address, "Fragile" labels (see attachment) on the top and on one side, and arrows indicating "This Side Up" (see attachment) on two adjacent sides.
12. Place custody seal evidence tape (see attachment) over front right and back left of the cooler lid and cover with clear plastic tape.

III. Shipping

1. Environmental samples will be shipped according to 40 CFR 761.65 (i)(3) and in accordance with current and applicable D.O.T. standards.
2. All samples will be delivered by an express carrier, allowing for sufficient time for analysis to be performed within the applicable holding time periods.
3. The following chain-of-custody procedures will apply to sample shipping:

- Relinquish the sample containers to the laboratory via express carrier. The signed and dated forms should be taped inside the top of the cooler. The express carrier will not be required to sign the chain-of-custody forms.
- When the samples are received by the laboratory, the laboratory personnel shall complete the chain-of-custody forms by signing and dating to acknowledge receipt of samples. The internal temperature of the shipping container is measured and recorded. The sample identification numbers on the containers are then checked to ensure that they are consistent with the chain of custody forms

Sample Shipping Label

	LimnoTech **734-332-1200**
Client/Source:	☐ **Grab** ☐ **Composite**
Site Name:	**Date:**
Sample #	**Time:**
Analysis:	**Preservatives:**
	Collected by:

Sample Custody Seal Label

LimnoTech **501 Avis Drive** **Ann Arbor, MI 48108**	Sealed by: _____ Date: _____ Time: _____

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Sample Chain of Custody Form

Limno-Tech, Inc.
Excellence in Environmental Engineering Since 1975

Check Originating Office

☐ Corporate Office
501 Avis Drive
Ann Arbor, MI 48108
(734) 332-1200 (phone)
(734)332-1212 (fax)

☐ Kalamazoo Field Office
2980 Business One Drive
Kalamazoo, MI 49001
(616) 226-0190 (phone)
(616) 226-0192 (fax)

CHAIN OF CUSTODY RECORD

Proj. No.	Project Name					Number of Containers							
Samplers: *(Signature)*													
Sta. No.	Date	Time	COMP	GRAB	Station Location								Remarks

Relinquished by: *(Signature)*	Date	Time	Received by: *(Signature)*	Relinquished by: *(Signature)*	Date	Time	Relinquished by: *(Signature)*	
Relinquished by: *(Signature)*	Date	Time	Received by: *(Signature)*	Relinquished by: *(Signature)*	Date	Time	Relinquished by: *(Signature)*	
Relinquished by: *(Signature)*	Date	Time	Received for Laboratory by: *(Signature)*	Date	Time	Remarks:		

Distribution: Original Accompanies Shipment; Copy to Coordinator Field Files

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Appendix B
Laboratory Standard Analytical Procedures (SAPs)

STANDARD OPERATING PROCEDURE

BIOCHEMICAL OXYGEN DEMAND
(5 Days, 20°C)

SM 5210 B

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Authorization/Approval:

C. Williams 6/6/13
Supervisor Date

6-7-13
QA Manager Date

6/6/13
Laboratory Director Date

Revision No.: R9

Effective Date: 6/7/13

Media: Water, Wastewater

Document No.: BA-WC-8

1.0 SCOPE AND APPLICATION:

1.1 The biochemical oxygen demand (BOD) test is used for determining the relative oxygen requirements of municipal and industrial wastewaters, aqueous, drinking water, saline/estuarine. Application of the test to organic waste discharges allows calculation of the effect of the discharges on the oxygen resources of the receiving water. Data from BOD tests are used for the development of engineering criteria for the design of wastewater treatment plants.

1.2 The BOD test is an empirical bioassay-type procedure which measures the dissolved oxygen consumed by microbial life while assimilating and oxidizing the organic matter present. The standard test conditions include dark incubation at 20°C for a specified time period (often 5 days). The actual environmental conditions of temperature, biological population, water movement, sunlight, and oxygen concentration cannot be accurately reproduced in the laboratory. Results obtained must take into account the above factors when relating BOD results to stream oxygen demands.

1.3 The reporting limit for BOD is 2000-µg/L.

2.0 SUMMARY OF METHOD:

2.1 An airtight bottle is filled to overflowing with sample and incubating it at 20°C for 5 days in the dark. Dissolved oxygen is measured initially and after incubation, and the BOD is computed from the difference between initial and final DO. Because the initial DO is determined shortly after the dilution is made, all oxygen uptake occurring after this measurement is included in the BOD measurement.

3.0 DEFINITIONS

3.1 A measure of the amount of oxygen consumed in the biological processes that break down organic matter in water. The greater the BOD, the greater the degree of pollution.

4.0 COMMENTS

4.1 Determination of dissolved oxygen in the BOD test may be made by use of either the Modified Winkler with Full-Bottle Technique or the Probe Method in this manual.

4.2 Additional information relating to oxygen demanding characteristics of wastewaters can be gained by applying the Total Organic Carbon and Chemical Oxygen Demand tests.

5.0 SAFETY

5.1 Always wear appropriate eye protection.
5.2 Wear gloves and wash hands frequently.

6.0 INTERFERENCES

6.1 Many things interfere with the BOD analysis:
- Any living organism that requires oxygen
- Any type of chemical that would kill the BOD organisms and give a false reading.
- Oils and gasoline: Oils can coat the probe resulting in an inaccurate reading and gasoline may ruin the probe.

7.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

7.1 Samples must be kept at 4°C or lower (near freezing) prior to analysis. Samples shipped to the laboratory must be on ice and within 24 hours of collection time.

7.2 Samples for BOD analysis may degrade significantly during storage between collection and analysis, resulting in low BOD values. Minimize reduction of BOD by analyzing sample promptly or by cooling it to near-freezing temperature during storage. However, even at low temperature, keep holding time to a minimum. Warm chilled samples to 20°C±3°C before analysis.

7.2.1 Grab Samples – If analysis is begun within 2 hour of collection, cold storage is unnecessary. If analysis not started within 2 hours of sample collection, keep sample

at or below 4°C from the time of collection. Do not start analysis more than 24 hours after grab sample collection.

7.2.2 Composite Samples – Keep samples at or below 4°C during compositing. Limit compositing period to 24 hours. Use the same criteria as for storage of grab samples, starting the measurement of holding time from end of compositing period. State storage time and conditions as part of the results. Start analysis within 48 hours of collection.

8.0 EQUIPMENT AND SUPPLIES

8.1 Incubation Bottles: 300-mL capacity with a ground glass stopper with a flared mouth. Clean bottles with a detergent, rinse thoroughly, and drain before use. As a precaution against drawing air into the dilution bottle during incubation, use a water-seal

8.2 Air Incubator: thermostatically controlled at 20 ± 1°C. Exclude all light to prevent possibility of photosynthetic production of dissolved oxygen.

8.3 DO probe - Calibrated daily before each use.

8.3.1 HACH HQ44d multi-meter with a HACH LDO probe LBOD101 (primary)
8.3.2 Orion Probe 9708 Dissolve Oxygen Probe (backup)

9.0 PROBE CALIBRATION

9.1 HACH HQ44d multi meter/HACH LDO probe LBOD 101:

1. Press power on meter.
2. Press calibration button.
3. Dry meter tip with a lint free Chem Wipe
4. Press "read" on the meter
5. Review calibration
6. Store calibration in meter. Ready to use.

9.2 ORION probe 9708 Dissolve Oxygen probe:

1. Check battery setting is 13.41 or greater.
2. Check zero setting. Use left know to adjust.
3. Check air setting. It should read 7.50. Use right knob to adjust.
4. Turn switch to H2O and begin using.

10.0 REAGENTS AND STANDARDS

Prepare reagents in advance but discard if there is any sign of precipitation or biological growth in the stock bottles.

10.1 BOD Nutrient Buffer Pillows, purchased in 3L or 6L preparation sizes, which contain:

10.1.1 Ammonium chloride.
10.1.2 Calcium chloride
10.1.3 Ferric chloride
10.1.4 Magnesium sulfate
10.1.5 Potassium phosphate, monobasic
10.1.6 Potassium phosphate, dibasic
10.1.7 Sodium phosphate, dibasic
10.1.8 De-mineralized water

10.2 BOD Seed: 1 Pill/500 mL reagent water. Stir for 1 hour.

10.3 Reagent water: 1 buffer pillow per 3/6 L. Bubble air through water for at least 20-30 minutes. Any longer can produce artificially high initial dissolved oxygen.

10.4 Acid and Alkali solutions , 1N, for neutralization of caustic or acidic waste samples.

- Acid - slowly and while stirring, add 28-mL concentrated sulfuric acid to distilled water. Dilute to 1-L.
- Alkali - Dissolve 40-g sodium hydroxide in distilled water. Dilute to 1-L.

10.5 Sodium sulfite solution: Dissolve 1.575-g Na_2SO_3 in 1000-mL distilled watr. This solution is not stable. Prepare daily.

10.6 Nitrification inhibitor, 2-chloro-6-(trichloromethyl)pyridine. Hach Co. Formula 2533.

10.7 Glucose-glutamic acid solution: Dry reagent grade glucose and reagent-grade glutamic acid at 103°C for 1 hour. Add 150-mg glucose and 150-mg glutamic acid to distilled water and dilute to 1 liter. Prepare fresh immediately before use.

10.8 Ammonium chloride solution: Dissolve 1.15-g NH_4Cl in about 500-mL distilled water, adjust pH to 7.2 with NaOH solution and dilute to 1-liter. Solution contains 0.3 mg N/mL.

10.9 Dilution water: Use distilled water for making sample dilutions. Setup two dilution water blanks (no seed added) to check the DI water and glassware.

11.0 PROCEDURE

11.1 Preparation of dilution water: 1 buffer pillow per 3/6 L.

- Test dilution water as a rough check on quality of unseeded dilution water and cleanliness of incubation bottles. Together with each batch of samples incubate a bottle of unseeded dilution water. Determine the initial and final DO. The DO uptake should not be more than 0.2-mg/L and preferable not more than 0.1-mg/L. Discard all dilution water with DO uptake greater than 0.2-mg/L and either eliminate source of contamination or select an alternate dilution water source.

Before use, bring dilution water temperature to 20±3°C. Saturate with DO by aerating with organic-free filtered air for 20-30 minutes. Any longer can produce artificially high initial dissolved oxygen.

11.2 Dilution water storage: Dilution water is not stored. Prepare dilution water as needed.

11.3 Glucose-glutamic acid (GGA) check: The BOD test is a bioassay and results can be influenced greatly by the presence of toxicants or by use of a poor seeding material. Distilled waters frequently are contaminated with copper, some sewage seeds are relatively inactive. Low results are always obtained with such seeds and waters. Check dilution water quality periodically, seed effectiveness, and analytical technique by making BOD measurements on a mixture of 150-mg glucose/L and 150-mg glutamic acid/L as a "standard" check solution. Determine the 5-day 20°C BOD of a 2% dilution of the GGA standard check solution using the techniques outlined in Section 10.4. Adjust concentrations of commercial mixtures to give 3-mg/L glucose and 3-mg/L glutamic acid in each GGA test bottle. Evaluate data as described in Section 12.0. Two GGA standards are prepared for calculations.

11.4 **Seeding:**

11.4.1 Seed source: It's necessary to have a population of microorganisms capable of oxidizing the biodegradable organic matter in the sample. Seed the dilution water by adding a population of microorganisms (Section 9.2).

11.4.2 Seed control: Determine the BOD of the seeding material as for any other sample. This is the seed control. Ideally make dilutions of seed such that the largest quantity results in at least 50% DO depletion. A plot of DO depletion , in mg/L, versus milliliters of seed for all bottles having a 2-mg/L depletion and a 1.0-mg/L minimum residual DO should present a straight line for which the slope indicated DO depletion per milliliter of seed. The DO-axis intercept is oxygen depletion caused by the dilution water and should be less than 0.1-mg/L (Section 10.1). Alternatively, divide DO depletion by volume of seed in milliliters for each seed control bottle having a 2-mg/L depletion and a 1.0-mg/L residual DO. Average the results for all bottles meeting minimum depletion and residual DO criteria. The DO uptake attributable to the seed added to each bottle should be between 0.6 and 1.0-mg/L but the amount of seed added should be adjusted from this range to that reuqired to provide GGA check results in the range of 198±30.5-mg/L. To determine DO uptake for a test bottle, subtract DO uptake attributable to the seed from total DO uptake (Section 11.1).

11.5 **Sample Pretreatment:** Check pH of all samples before testing.

11.5.1 Samples containing caustic alkalinity (pH>8.5) or acidity (pH<6.0) - Neutralize samples to pH 6.5 to 7.5 with sulfuric acid or sodium hydroxide of such strength that the quantity of reagent does not dilute the sample by more than 0.5%. The pH of the dilution water is not affected by the lowest sample dilution. Seed samples that have been pH adjusted.

11.5.2 Samples containing residual chlorine compounds - If the sample has been chlorinated but no detectable chlorine residual is present, seed the dilution water. If residual chlorine is present, dechlorinate sample and seed the dilution water. Chlorinated/dechlorinated samples are not tested until the dilution water has been seeded. Destroy chlorine residual by adding Na_2SO_3 solution. Determine required volume of Na_2SO_3 solution on a 100-mL to 1000-mL portion of neutralized sample by adding 10-mL of 1+1 acetic acid or 1+50H_2SO_4, 10-mL potassium iodide (KI) solution (10-gms/100-mL0 per 1000-mL portion, and titrating with Na_2SO_3 solution to the starch-iodine end point for residual. Add to neutralized sample the relative volume of Na_2SO_3 solution determined by the above test, mix, and after 10 - 20 minutes check sample for residual chlorine.

11.5.3 Samples that are supersaturated with DO- Samples containing more than 9 mg DO/L at 20°C may be encountered in cold waters or in water where photosynthesis occurs. To prevent loss of oxygen during incubation of such samples, reduce DO to saturation at 20°C by bringing sample to about 20°C in partially filled bottle while agitating by aerating with clean, compressed air.

11.5.4 Sample temperature adjustment - bring samples to 20$\pm$1°C before making dilutions.

11.5.5 Nitrification inhibition - Samples that may require nitrification inhibition include biologically treated effluents, samples seeded with biologically treated effluents, and river waters. Add 3-mg 2-chloro-6-(trichloro methyl) pyridine (TCMP) to each 300-mL bottle before capping or add sufficient amounts to the dilution water to make a final concentration of 10-mg/L .

11.6 Dilution Technique - Make several dilutions of sample that will result in a residual DO of at least 1-mg/L and a DO uptake of at least 2-mg/L after a 5 day incubation. In the absence of prior knowledge of the sample, use the following dilutions: 0.0 to 1% for strong industrial wastes, 1 to 5% for raw and settled wastewater, 5 to 25% for biologically treated effluent, and 25 to 100% for polluted river waters. Prepare dilutions directly in BOD bottles. When dilutions are prepared directly in BOD bottles and seeding is necessary, add seed directly to the BOD bottles.

11.6.1 Dilutions prepared directly in BOD bottles - Use a wide tip volumetric pipette, add the desired sample volume to individual BOD bottles of known capacity. Add seed material to BOD bottle. Fill bottles with enough dilution water, seeded if necessary, so that insertion of stopper will displace all air, leaving no bubbles. For dilutions greater than 1:100 make a primary dilution in a graduated cylinder before making final dilution in the bottle. Determine initial DO on this bottle and replace any displaced contents with dilution water to fill the bottle. Stopper tightly, water-seal and incubated for 5 days at 20°C. Rinse DO electrode between determinations to prevent cross-contamination. Determine the initial DO on all sample dilutions, dilution water blanks, and where appropriate, seed controls.

11.7 Determination of Initial DO - Determine initial DO within 30 minutes of preparing dilution and measuring initial DO.

11.7.1 Calibrate Electrode:

- With the electrode in the Off position, set pH meter to read 7.00.
- With the electrode in the zero postion, turn left knob on electrode to read 0.00.
- With the electrode in the air position, turn right knob on electrode to read 7.50.
- Warm chilled samples to 20±1°C before analysis.

11.8 Dilution Water Blank - A dilution water blank is used as a rough check on quality of unseeded dilution water and cleanliness of incubation bottles. With each batch of samples (≤20 samples), incubate a bottle of unseeded dilution water. Determine initial and final DO. The DO uptake should not be more than 0.2 mg/L. Discard all dilution water having a DO uptake greater than 0.2 mg/L and either eliminate source of contamination or select an alternate dilution water source.

11.9 Incubation - Incubate at 20°C±1°C BOD bottles containing dilutions, seed controls, dilution water blanks and GGA checks. Water-seal bottles.

11.10 Determination of final DO - After 5-day incubation, determine DO in sample dilutions, blanks, and checks.

12.0 CALCULATIONS

12.1 For each bottle meeting the 2.0 mg/L minimum DO depletion and the 1.0 mg/L residual DO, calculate BOD_5 as follows:

When dilution is not seeded:

$$BOD_5, mg/L = \frac{D_1 - D_2}{P}$$

When dilution water is seeded:

$$BOD_5, mg/L = \frac{(D_1 - D_2) - (B_1 - B_2)f}{P}$$

Where:

D_1 = DO of diluted sample immediately after preparation, mg/L
D_2 = DO of diluted sample after 5 day incubation at 20°C, mg/L
P = Decimal volumetric fraction of sample used
B_1 = DO of seed control before incubation, mg/L
B_2 = DO of seed control after incubation, mg/L
f = ratio of seed in diluted sample to seed in seed control = (% seed in diluted sample)/(%seed in seed control)

12.2 Report results as CBOD if nitrification is inhibited.

12.3 If more than one sample dilution meets the criteria of a residual DO of at least 1-mg/L and DO depletion of 2-mg/L and there is no evidence of toxicity at higher sample concentrations or the existence of an obvious anomaly, average the results in the acceptable range.

12.4 In the above calculations, do not make corrections for DO uptake by the dilution water blank during incubation. This correction is unnecessary if dilution water meets the blank criteria stipulated above. If the dilution water does not meet these criteria, proper corrections are difficult; do not record results or, as a minimum, flag them as not meeting quality control criteria.

13.0 QUALITY CONTROL

13.1 A GGA check standard is analyzed per batch of samples. The criteria is $\pm$10%. If criteria is not met, samples are reported and qualified on the final reports.

13.2 A duplicate is performed in each batch. A batch is $\leq$20 samples. The acceptable criteria is $\pm$20%. If criteria is not met, samples are reported and qualified on the final report.

13.3 A method blank (dilution water blank) in analyzed with each batch of samples. The DO uptake should not be more than 0.2 mg/L and preferably not more than 0.1 mg/L. A batch is $\leq$20 samples. If method blank criteria is not met, samples are reported out and qualified on the final report.

14.0 METHOD PERFORMANCE

14.1 There is no acceptable procedure for determining the accuracy of the BOD test.

15.0 CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

15.1 If dilution water blank does not meet the criteria of DO uptake at or below 0.2-mg/L, flag the samples as qualified, not meeting quality control criteria. If dilution water source above 0.2-mg/L DO uptake, eliminate source of contamination or select an alternate dilution water source.

15.2 If GGA check does not meet criteria above, qualify data as not meeting quality control criteria.

16.0 METHOD REFERENCE

16.1 Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998.

17.0 WASTE MANAGEMENT

17.1 After the BOD samples have had their final reading (5 days), the samples are discarded down the drain with adequate water. If the samples contain oil or solvents, the sample may be discarded in the waste drums (See SOP BA013, Sample Disposal Procedures).

STANDARD OPERATING PROCEDURE

INORGANIC IONS BY ION CHROMATOGRAPHY

EPA 300.0 r2.1

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Authorization/Approval:

C. Williams 7/16/14
Supervisor Date

7-17-14
QA Manager Date

7/16/14
Laboratory Director Date

Revision No.: R13

Effective Date: 7/18/14

Media: Drinking Water, Water, Wastewater

Document No.: BA-IC-1

1.0 SCOPE AND APPLICATION:

1.1 This method addresses the sequential determination of the anions chloride (Cl), fluoride (F), bromide (Br), nitrate (NO_3), nitrite (NO_2), and sulfate (SO_4).

	Reporting Limit (µg/L)
Chloride	1000
Fluoride	100
Nitrate	50
Nitrite	50
Sulfate	1000

1.1 This method is applicable to drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, aqueous, saline/estuarine, non-aqueous liquid, reagent waters, and leachates (when no acetic acid is used).

1.2 The minimum detectable concentrations are in the range of 100 µg/L for F and Br, 1000 µg/L for Cl and SO_4, and 10 µg/L for NO_3 and NO_2.

2.0 SUMMARY OF METHOD:

2.1 A 5-mL volume of sample is injected into the ion chromatograph to flush and fill a constant volume sample loop. The sample is then injected into a stream of KOH eluent.

2.2 The sample is pumped through an ion exchange column and into a conductivity detector. Ions are separated into discrete bands based on their affinity for the exchange sites of the resin. The separated anions in their acid form are measured using an electrical-conductivity cell. Anions are identified based on their retention times compared to known standards.

Quantitation is accomplished by measuring the peak area and comparing it to a calibration curve generated from known standards.

3.0 INTERFERENCES

3.1 Any species with retention time similar to that of the desired ion will interfere. Large quantities of ions eluting close to the ion of interest will also result in interference. Separation can be improved by adjusting the eluent concentration. Sample dilution and/or the use of the method of standard additons can also be used. Two common species, formate and acetate, elute between fluoride and chloride.

3.2 Bromide and nitrate elute very close together and are potential interferences for each other.

3.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts.

4.0 DEFINITIONS

4.1 **Calibration Blank (CB)** -- A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes, internal standards, or surrogate analytes.

4.2 **Calibration Standard (CAL)** -- A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

4.3 **Field Duplicates (FD)** -- Two separate samples collected at the same time and placed under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of field duplicates indicate the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

4.4 **Instrument Performance Check Solution (IPC)** -- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

4.5 **Laboratory Fortified Blank (LFB)** -- An aliquot of reagent water or other blank matrices to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

4.6 **Laboratory Fortified Sample Matrix (LFM)** -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

4.7 **Laboratory Reagent Blank (LRB)** -- An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

4.8 **Linear Calibration Range (LCR)** -- The concentration range over which the instrument response is linear.

4.9 **Material Safety Data Sheet (MSDS)** -- Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

5.0 APPARATUS AND MATERIALS

5.1 Ion Chromatograph – Dionex ICS-2100, delivering 1.0-mL of eluent per minute at a pressure of 2,300-psi. The chromatograph is equipped with an injection valve, a 25.0-µL sample loop, and set-up with the following components:

5.1.1 Separator column - A 4x50-mm AG18 guard column and a 4x250-mm AS18 analytical column that is used for resolving F, Cl, NO_3, Br, NO_2 and SO_4.

5.1.2 Detector – DS6 Heated Conductivity Detector.

5.1.3 Pump – delivers a constant flow of 1.0 ml/min throughout the test and tolerating a pressure of 2,000 to 3,000-psi.

5.2 Computer – records the detector output and integrates the area under the chromatogram.

5.3 Eluent Generator Cartridge – Dioxex EGC III KOH RFIC Eluent Generator Cartridge.

5.4 Analytical balance –capable of weighing to the nearest 0.001 gram.

5.5 Class A volumetric flasks and beakers.

5.6 Pipets – Class A

6.0 REAGENTS AND STANDARDS

6.1 Reagent grade chemicals are used in all tests.

6.2 Reagent water- Deionized water free of the anions of interest. Water contains particles no larger than 0.20 microns.

6.3 Eluent – Degassed Dionized (DI) Water:

6.4 Stock solutions (1,000 mg/L) of the anions of interest:

6.4.1 Prepare a high-range standard solution by diluting the volumes of each anion being tested together with 1 liter reagent water (dried at 105°C for 30 minutes)

- Fluoride: Dissolve 2.2100g sodium fluoride (NaF) into reagent water and dilute up to 1 liter.
- Chloride: Dissolve 1.649g sodium chloride (NaCl) in reagent water and dilute up to 1 liter.
- Nitrite: Dissolve 4.93g sodium nitrite ($NaNO_2$) in reagent water and dilute up to 1 liter.
- Nitrate: Dissolve 7.22g potassium nitrate (KNO_3) in reagent water and dilute up to 1 liter.
- Sulfate: Dissolve 1.479g sodium sulfate [$Na_2(SO_4)$] in reagent water and dilute to 1 liter.

6.4.2 Summary of Ion Concentrations in I.C. Standards (All concentrations in the following chart are in mg/L or ppm)

ION	STD1	STD2	STD3	STD4	STD5	STD6	STD7	STD8
F	0.10	0.50	1.00	5.0	10	20		
Cl	1.00	5.00	10.00	50.0	100	200	300	500
NO_2	0.01	0.05	0.10	0.50	1.00	2.0	5.0	10
NO_3	0.01	0.05	0.10	0.50	1.00	2.0	5.0	10
SO_4	1.00	5.00	10.00	50.0	100	200	300	500

6.5 Stability of Standards – stock standards are stable for at least 1 month when stored at 4°C. Dilute working standards are prepared weekly, except those that contain nitrite, which are prepared fresh daily. Method standards (laboratory control standards LCS) are prepared fresh daily.

6.6 Matrix Spike and Method Standards - Prepare the spiking and method standard solution: 100µL of spiking solution (#18) to 5 mL reagent water. The following concentrations are Fluoride (5.0 mg/L), Chloride (50 mg/L), Nitrite (1.0 mg/L), Nitrate (1.0 mg/L), and Sulfate (50 mg/L).

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 Samples are collected in plastic or glass bottles.
7.2 The samples are analyzed as soon as possible after collection.

Analyte	Preservation	Holding Time
Chloride	None required	28 days
Fluoride	None required	28 days
Nitrate	Cool to 4°C	48 hours
Nitrite	Cool to 4°C	48 hours
Sulfate	Cool to 4°C	28 days

8.0 PROCEDURE

8.1 Calibrate the instrument using the concentrations listed in the Chart in section 6.4.2 above. Calibration utilizes linear regression. Calibration of the Ion Chromatograph is not required on a daily basis. Calibration is verified for every run by analyzing an independent certified check standard to an accuracy of ±10%.

8.2 Sample Preparation - any dilutions required in analyzing samples are made with reagent water.

8.3 A laboratory reagent blank and a method standard are at the beginning of the run to verify the curve, after every 10th sample and at the end of the analytical run. The curve is verified if all analytes are within ±10%. If not within +10%, verification is repeated using fresh calibration standards. If results still greater than ±10%, a new curve is prepared.

8.4 Sample Analyses

8.4.1 Start the pump by selecting "PUMP" on the control panel window box.

8.4.2 Create a sequence by clicking on "Window" then "Browser". Use the previous days sequence as a template. Select file then "save as" to change the sequence name to the current date and select "save raw data" (unless re-calibrating). The sample list includes a blank, laboratory control sample (LCS or method standard), independent check standard, sample(s), and a matrix spike/matrix spike duplicate for each batch of 10 samples or less. All entries must have Anion Program Oct under the program column, QNT under the method column and single under the status column.

8.4.3 Select "BATCH" and then "START" to run sequence. System must be stabilized before analysis begins due to system sitting idol overnight. Analyze at least 3 LCSs until the system stabilizes.

8.4.4 The width of the retention time window used to make identifications is based on measurements of actual retention time variations of standards over the course of a day.

8.4.5 If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and re-analyze.

8.4.6 If identification of specific anions is questionable, spike the sample with an appropriate amount of standard and re-analyze.

NOTE: Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. In some cases, this peak migration can produce poor resolution or misidentification.

8.5 Calculations – all calculations of the sample concentration are performed by the computer and the analyst needs only verify the peak identification and the integration baseline.

9.0 QUALITY CONTROL

9.1 Initial Demonstration of Performance

9.1.1 Linear Calibration Range (LCR) – The curve is determined every 6 months or whenever a significant change in instrument response is observed. The verification of linearity must use a minimum of a blank and 3 standards. If any verification data exceeds the initial values by ±10%, linearity is re-established.

9.1.2 Quality Control Sample (QCS) – Verify the calibration standards and acceptable instrument performance with the analysis of a QCS on a per run basis. The determined concentration must be within ±10% of the stated values. If not, re-calibrate.

9.1.3 Method Detection Limit (MDL) – MDLs are established for all analytes using reagent water fortified at a concentration of 2-3 times the estimated instrument detection limit. Seven replicates are analyzed and calculated (See BA SOP# BA003 for information on performing an MDL study). MDLs for this method are determined every 6 months, whenever a new operator begins work, or whenever there is significant change in the background or instrument response. Current MDL studies are located within the laboratory.

9.2 Laboratory Performance

9.2.1 Laboratory Blank/Method Blank (LRB) – The laboratory analyzes at least one blank with each batch of samples. Blank values that exceed the MDL could indicate laboratory or reagent contamination and corrective actions are taken before continuing analyses.

9.2.2 Laboratory Fortified Blank/Method Standard (LFB) – The laboratory analyzes at least one method standard with each batch of samples. If the recovery of any analyte falls outside the required control limits of **90-110%**, the analyte is out of control and the source of the problem must be identified and resolved before continuing analyses.

The laboratory uses the method standard data to assess laboratory performance against the required control limits of 90-110%. Control limits are generated in the laboratory and are within the 90-110%. If the control limits are outside the 90-110% range, the required control limits are used (i.e., internally generated limits cannot be less restrictive than the method specific limits).

9.3 Instrument Performance Check Solution (IPC)

Analyze the IPC (a mid-range check standard) and a blank immediately following daily calibration, after every tenth sample and at the end of the sample run. The IPC verifies the instrument is within ±10% of calibration and subsequent analysis. If the calibration is not verified within ±10%, reanalyze the IPC. If second analysis is outside the ±10%, sample analysis is discontinued and cause determined and/or instrument re-calibrated. All samples following the last acceptable IPC solution are reanalyzed. The analysis of the calibration blank and IPC solution is kept on file with the sample analysis date.

9.4 Analyte Recovery and Data Quality

9.4.1 Laboratory Fortified Sample Matrix/Matrix Spike – The laboratory fortifies 10% of routine samples with a known amount of analyte. The analyte concentration is equal to a mid-range standard. The matrix spike amount is the same concentration that is used in the Method Standard.

9.4.2 Calculate the % recovery of the Matrix spike:

$$R = \frac{Cs - C}{S} \times 100$$

where: R = percent recovery
Cs= fortified sample concentration
C = sample background concentration
S = concentration equivalent of analyte added to the sample

9.4.3 Matrix spikes must be within **80-120%** or better (depending on internally derived control limits). If the MS is out for any of the analytes but the method standard shows in-control for that compound, the recovery problem is judged to be either matrix or solution related, not system related.

10.0 SAFETY

10.1 The toxicity or carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

10.2 Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) is available to all personnel involved in the chemical analysis.

10.3 The following chemicals have the potential to be highly toxic or hazardous, consult MSDS: Sulfuric acid

11.0 METHOD PERFORMANCE

11.1 The method detection limit (MDL) is the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. Current MDL studies are located in the Quality Assurance Office Training Files for each analyst.

12.0 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

12.1 Linear Calibration Range (LCR)- Verified every 6 months. If data exceeds $\pm$10%, reestablish linearity.

12.2 Verify the QCS quarterly. If the determined concentrations are not within +10%, performance of the determinative step is unacceptable. Identify the source of the problem and correct before proceeding with sample analysis.

12.3 If Laboratory Reagent Blank (LRB) contains values of target analytes that exceed the MDL, contamination is suspected and corrective actions are taken before continuing with sample analysis.

12.4 Laboratory Fortified Blank (LFB) - Analyze one LFB per batch of samples. If falls outside the ±10% control range, analyte is out of control. Identify the source of the problem and resolve it before continuing with analysis.

12.5 If IPC falls outside the ±10% range, reanalyze it. If fails again, discontinue sample analysis, determine the cause and re-calibrate.

12.6 Matrix Spikes (LFM) - If recovery falls outside the ±20% range and the laboratory performance for that analyte is shown to be in control, the recovery problem encountered with the LFM is judged to be either matrix or solution related, not system related.

13.0 POLLUTION PREVENTION

13.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

14.0 METHOD REFERENCE

14.1 Methods For Analysis of Water, Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Revision 2.1, August 1993.

15.0 WASTE MANAGEMENT

15.1 Excess Reagents, samples, extracts and method process wastes are characterized and disposed of in an acceptable manner. For more information on disposal, see BA013, Sample Disposal Procedure.

STANDARD OPERATING PROCEDURE

TOTAL KJELDAHL NITROGEN

(TKN, Semi-Automated Colorimetry)

SM 4500-N_{org}-B

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Authorization/Approval:

C. Williams 7/16/14
Supervisor Date

7-18-14
QA Manager Date

7/16/14
Laboratory Director Date

Revision No.: R9

Effective Date: 7/18/14

Media: Water, Wastewater

Document No.: BA-WC-24

1.0 SCOPE AND APPLICATION:

1.1 This method covers the determination of total Kjeldahl nitrogen in drinking, ground, and surface waters, domestic and industrial wastes. The procedure converts nitrogen components of biological origin such as amino acids, proteins and peptides to ammonia, but may not convert the nitrogenous compounds of some industrial wastes and some refractory tertiary amines.

1.2 The applicable range is 100 to 5,000-µg/L TKN. The range may be extended with sample dilution.

1.3 The reporting limit for TKN is 100-µg/L.

2.0 SUMMARY OF METHOD

2.1 The sample is heated in the presence of sulfuric acid, H_2SO_4, for 3½ hours. The residue is cooled, diluted to 25-mL and analyzed for ammonia.

2.2 Total Kjeldahl nitrogen is the sum of free-ammonia and organic nitrogen compounds which are converted ammonium sulfate $(NH_4)_2SO_4$, under the conditions of digestion described.

2.3 Reduced volume versions of this method that use the same reagents and molar ratios are acceptable provided they meet the quality control and performance requirements stated in the method.

3.0 INTERFERENCES

3.1 High nitrate concentrations (10x or more than the TKN level) result in low TKN values. If interference is suspected, samples should be diluted and reanalyzed.

3.2 Method interference may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that bias analyte response.

4.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

4.1 Samples should be collected in plastic or glass bottles. All sample containers must be prewashed and thoroughly rinsed with reagent water. Volume collected should be sufficient to insure a representative sample, allow for replicate analysis, and minimize waste disposal.

4.2 Samples must be preserved with H_2SO_4 to a pH<2 and cooled to 4°C at the time of collection.

4.3 Samples should be analyzed as soon as possible after collection. If storage is required, preserved samples are maintained at 4°C and may be held up to 28 days.

5.0 APPARATUS

5.1 Analytical Balance, capable of weighing to the nearest 0.0001 g.

5.2 Glassware – Class A volumetric flasks and pipettes as required.

5.3 Block digestor with tubes.

5.4 Konelab 20

6.0 REAGENTS AND STANDARDS

6.1 Reagent water: Ammonia free distilled deionized water, free of the analyte of interest. ASTM Type II.

6.2 Digestion Solution: Dissolve 134-g K_2SO_4 and 7.3-g $CuSO_4$ in 800-mL of reagent water. Carefully add 134-mL concentrated H_2SO_4. When the solution has cooled to room temperature, dilute the solution to 1-L with reagent water. Mix well.

6.3 Sodium Salicylate/Sodium Nitroprusside Solution: Dissolve 15-g of sodium salicylate (salicylic acid sodium salt) and 0.03-g of sodium nitroprusside (sodium nitroferricyanide dihydrate $Na_2Fe((N)_5NO{\cdot}2H_2O)$ in 60-mL reagent water. Dilute up to 100-mL.

6.4 Sodium Hypochlorite: Dilute 6-mL of sodium hypochlorite solution (Chlorox bleach) to 100-mL with reagent water.

6.5 NaOH Stock: Dissolve 20-g of NaOH in 90-mL of reagent water and dilute up to 100-mL.

6.6 Sodium Potassium Tartrate Stock: Dissolve 20-g of sodium potassium tartrate in 80-mL of reagent water. Dilute up to 100-mL.

6.7 Stock Buffer: Dissolve 13.4-g of sodium phosphate dibasic heptahydrate in 80-mL of reagent water. Add 2.0g of sodium hydroxide and dilute up to 100-mL.

6.8 Working Buffer: Add 25-mL of stock sodium potassium tartrate solution to 20mL of stock buffer solution and mix well. Add 25-mL of sodium hydroxide solution and dilute to 100-mL with reagent water.

6.9 TKN Special Diluent: Digest a blank with each batch of samples by adding 5-mL of digestion solution to 25-mL reagent water.

6.10 Hengar Granules.

7.0 CALIBRATION AND STANDARDIZATION

7.1 Prepare a series of 6 standards, covering the desired range, and a blank by diluting suitable volumes of standard solution with reagent water.

7.1.1 0.10, 0.25, 0.50, 1.00, 2.00 & 5.00-ppm standards.

7.2 Process standards and blanks as described in Section 8.0.

7.3 Place appropriate standards in the sampler in order of increasing concentration and perform analysis.

7.4 A standard curve is prepared by the Konelab. It plots instrument response against concentration values. The curve must have a correlation coefficient of at least 0.995 or the curve must be reanalyzed.

7.5 After calibration has been established, it must be verified by the analysis of an independent external reference quality control standard (ERA standard). If the measurements exceed $\pm$10% of the established quality control sample value, the analysis should be terminated and the instrument recalibrated. After recalibration, the new calibration must be verified before continuing analysis. Periodic reanalysis of the 1.00-ppm standard is used as a continuing calibration check.

8.0 PROCEDURE

8.1 Pipette 25-mL of sample, standard or blank in the digestor tube.

8.2 Add 5 mL of digestion solution and mix with a vortex mixer.

8.3 Add 2-4 henger granules. NOTE: An excess of chips may cause the sample to boil over.

8.4 Place tubes in block digestor preheated to 160°C and maintain temperature for 1 hour.

8.5 After one hour, put a cold finger in each tube and continue to heat for 2½ hours (380°C must be maintained for 30 minutes).

8.6 Remove digestion tubes, cool and dilute with 25-mL reagent water.

8.7 Place standards in order of increasing concentration with calibration check blank (CCB) and calibration check verification (CCV) in Konelab sample tray.

8.8 Calibrate the instrument before samples are analyzed.

8.9 After calibration has been evaluated/accepted, load samples in sample trays and analyze.

9.0 CALCULATION

9.1 Prepare a standard curve by plotting absorbance of standards against their concentration values. Use linear regression to compute concentrations of samples by comparing sample absorbance with

the standard curve. Multiply the answer by appropriate dilution factor. The curve must have a correlation coefficient of at least 0.995 or the curve must be reanalyzed.

9.2 Report only those values that fall between the lowest and the highest calibration standards. Samples that exceed the highest standard are diluted and reanalyzed.

9.3 Report results in µg-N/L.

10.0 QUALITY CONTROL

10.1 Initial Demonstration of Performance

10.1.1 A linear calibration range must be determined initially and verified every 6 months or whenever a significant change in instrument response is observed. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by +10%, linearity must be re-established.

10.1.2 Quality Control Standard (QCS) – When beginning the use of this method, on a quarterly basis, or as required to meet data quality needs, verify the calibration standards and analyses of a QCS (also called an independent secondary reference standard). If the determined concentrations are not within ±10% of the stated values, performance of the determinative step of the method unacceptable.

10.1.3 Method Detection Limit (MDL) – MDLs must be established for all analytes, using reagent water that has been fortified at a concentration of 2-3 times the estimated instrument detection limit. For more information on conducting an MDL study, see SOP #BA003.

10.2 Assessing Laboratory Performance (corrective actions):

10.2.1 Method Blank – One method blank is analyzed with each batch of samples. Data produced are used to assess contamination from the laboratory environment. Acceptance criteria for the method blank must be below the required reporting limit, ideally less than the method detection limit. If the method blank fails this criteria, re-prep the series of 7 standards and method blank and re-analyze. Corrective action is taken and documented for all method blank failures, even if associated data is reported with qualification.

10.2.2 Method Standard – One method standard is analyzed with each batch of sample. Calculate the accuracy as percent recovery. If the recovery falls outside the required limits of 90-110%, that analyte is judged out of control and the source of the problem should be identified and resolved before continuing analyses.

10.2.3 When sufficient internal performance data become available, control limits are established in-house. The laboratory control limits must be equal to or better than the required control limits of 90-110%.

10.2.4 Instrument Performance Check Solution – For all determinations, the laboratory must analyze the IPC and a calibration blank immediately following daily calibration, after every 10th sample, and at the end of the sample run. The IPC solution and calibration blank immediately following the calibration must verify that the instrument is within ±10% of calibration. Subsequent analyses of the IPC solution must verify the calibration is still within ±10%. If the calibration cannot be verified within the specified limits, reanalyze the IPC solution. If the second analysis of the IPC solution confirms calibration to be outside

the limits, sample analysis must be discontinued, the cause determined and/or in the case of drift the instrument recalibrated. All samples following the last acceptable IPC solution must be reanalyzed.

10.3 Assessing Analyte Recovery and Data Quality

103.1 Laboratory Fortified Sample Matrix (LFM)/Matrix Spike: A minimum of 10% of routine samples are spiked with a known amount of analyte. The added analyte should be the same as that used in the method standard.

103.2 Calculate the percent recovery and compare with a 90-110% range.

$$\% \text{ Recovery} = \frac{Cs - C}{s} \times 100$$

where:
R = percent recovery.
Cs = fortified sample concentration.
C = sample background concentration.
S = concentration equivalent of analyte added to sample.

10.3.3 If the recovery of the analyte is outside the range of 90-110%, it is reanalyzed. If it fails a second time and the method standard shows acceptable recoveries, the matrix spike is judges to be either matrix or solution related, not system relate.

11.0 METHOD PERFORMANCE

11.1 The method detection limit (MDL) is the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. Current MDL studies are located in the Quality Assurance Office Training Files for each analyst.

12.0 POLLUTION PREVENTION

12.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

13.0 METHOD REFERENCE

13.1 Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998, American Public Health Association.

14.0 WASTE MANAGEMENT

14.1 Excess Reagents, samples, extracts and method process wastes are characterized and disposed of in an acceptable manner. For more information on disposal, see BA013, Sample Disposal Procedure.

TKN

Laboratory
Analyzer User

Date : 2012-07-18
Time : 09.31

Full name	TKN SM 4500-Norg B	Test In Use	YES		
Online Name			LOW	HIGH	
Test type	Photometric	Test limit	*	50.000	mg/L
Result unit	mg/L	Initial absorbance	*	*	A
Number of Decim.	3	Dilution limit	*	5.0000	mg/L
		Secondary dil 1+	0.0	9.0	
		Critical limit	*	*	mg/L
		Reflex test limit	*	*	mg/L

Reflex test

Acceptance	Manual	Reference class	LOW	HIGH	In Use
Dilution 1+	0.0				
Sample type		Correction factor	1.00		
		Correction bias	0.00	mg/L	
Calibration type	Linear				
Repeat time (d)	0	Abs error (mA)		*	
Points/cal.	Single	Rel error (%)		*	
Acceptance	Manual				
Response limit (mA)	MIN	MAX			
	*	*			
Bias correction in use	NO				
Cd reduction	NO				
Type of Calibrators	Separate				

Calibrator	Conc.	Dil. ratio
TKN-0	0.000	1+0.0
TKN-0.1	0.100	1+0.0
TKN-0.25	0.250	1+0.0
TKN-0.50	0.500	1+0.0
TKN-1.0	1.000	1+0.0
TKN-2.0	2.000	1+0.0
TKN-5.0	5.000	1+0.0

Manual QC in Use	YES	Routine QC in Use		YES	
Acceptance	Manual	Interval	Requests	10	
		Additional condition		NO	

Control	Mean	SD	Control	Mean	SD
CCB-TKN	0.00	0.10	CCB-TKN	0.00	0.10
CCV-TKN	1.00	0.10	CCV-TKN	1.00	0.10

Rules in Use	1:1.0*SD	Rules in Use	1:1.0*SD
Blank	YES		
		Normal cuvette	
Reagent	TKN Buffer	Volume (ul)	80
Disp. with	Extra	Add. Volume (ul)	20
Wash reagent	None		

Test definition AquaKem 6.5 Page:

TKN Laboratory
Analyzer User

Date : 2012-07-18
Time : 09.31

Sample		Volume (ul)	32
Disp. with	Extra	Add. Volume (ul)	20
Dilution with	Special	Wash reagent	None
Raw Sample			
Disp. with	Extra	Add. Volume (ul)	20
Special diluent	TKN Dig Bl		
Disp. with	Extra	Add. Volume (ul)	20
Measurement	End point	Blank	
Resp. Min(A)	*	Resp. Max(A)	*
Reagent	TKN Salicy	Volume (ul)	32
Disp. with	Extra	Add. Volume (ul)	20
Wash reagent	None		
Incubation		Time (sec)	120
Reagent	TKN Hypoch	Volume (ul)	32
Disp. with	Extra	Add. Volume (ul)	20
Wash reagent	None		
Incubation		Time (sec)	600
Measurement	End point		
Wavelength (nm)	660 nm	Side wavel. (nm)	None
Meas. type	Fixed timing		

STANDARD OPERATING PROCEDURE

PHOSPHORUS, Total

SM4500-PE/HACH 8190/8048

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Authorization/Approval:

C. Williams 6/22/10
Supervisor Date

6/24/10
QA Manager Date

6/23/10
Laboratory Director Date

Revision No.: R8

Effective Date: 6/25/10

Media: Water, Waste

Document No.: BA-WC-18

1.0 SCOPE AND APPLICATION:

1.1 This method includes the determination of total phosphorus in drinking, surface, and saline waters, domestic and industrial wastes, sludge, aqueous, drinking water, and saline/estuarine.

1.2 This method is based on reactions that are specific for the orthophosphate ion. Thus, depending on the prescribed pre-treatment of the sample, the various forms of phosphorus given in Figure 1 may be determined.

1.3 The applicable range is 10 to 2000 µg/L. The range may be extended with sample dilution.

1.4 The reporting limit for Phosphorus is 10-µg/L for water and 100-µg/Kg for soils/sludges.

2.0 SUMMARY OF METHOD

2.1 Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex by ascorbic acid. The color is proportional to the phosphorus concentration.

2.2 Polyphosphates (and some organic phosphorus compounds) may be converted to the orthophosphate form by sulfuric acid hydrolysis. Organic phosphorus compounds may be converted to the orthophosphate form by persulfate digestion.

2.3 See Figure 1. Analytical scheme for differentiation of phosphorus forms.

3.0 DEFINITIONS

3.1 Total Phosphorus (P)- All of the phosphorus present in the sample, regardless of form, as measured by the persulfate digestion procedure.

3.1.1 Total Orthophosphate (P, ortho)- inorganic phosphorus [$(PO_4)^{-3}$] in the sample as measured by the direct colorimetric analysis procedure.

3.1.2 Total Hydrolyzable Phosphorus (P, hydro) - phosphorus in the sample as measured by the sulfuric acid hydrolysis procedure, and minus pre-determined orthophosphates. This hydrolyzable phosphorus includes polyphosphorus. [$(P_2O_7)^{-4}$, $(P_3O_{10})^{-5}$, etc.] plus some organic phosphorus.

3.1.3 Total Organic Phosphorus (P, org) - phosphorus (inorganic plus oxidizable organic) in the sample measured by the persulfate digestion procedure, and minus hydrolyzable phosphorus and orthophosphate.

3.2 Dissolved Phosphorus (P-D)- All of the phosphorus present in the filtrate of a sample filtered through a 0.45 micron filter and measured by the persulfate digestion procedure.

3.2.1 Dissolved Orthophosphate (P-D, ortho)- as measured by the direct colorimetric analysis procedure.

3.2.2 Dissolved Hydrolyzable Phosphorus (P-D, hydro) - as measured by the sulfuric acid hydrolysis procedure and minus pre-determined dissolved orthophosphates.

3.2.3 Dissolved Organic Phosphorus (P-D, org)- as measured by the persulfate digestion procedure and minus dissolved hydrolyzable phosphorus and orthophosphate.

4.0 INTERFERENCES

4.1 No interference is caused by copper, iron, or silicate at concentrations many times greater than their reported concentration in sea water. However, high iron concentrations can cause precipitation of and subsequent loss of phosphorus.

4.2 The salt error for samples ranging from 5 to 20% salt content was found to be less than 1%.

4.3 Arsenate is determined similarly to phosphorus and should be considered when present in concentrations higher than phosphorus. However, at concentrations found in sea water, it does not interfere.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable.

6.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

6.1 Sample containers can be plastic or glass.

6.2 Water samples are preserved with 2mL of concentrated H_2SO_4 per liter of sample collected and refrigerated at 4°C for total phosphorus. No preservative is added for determination of phosphorus forms.

7.0 EQUIPMENT, SUPPLIES, AND APPARATUS

7.1 Spectrophotometer, suitable for measurement at 650 or 890-nm with a light path of 1 cm or longer.

7.2 Glassware is purchased as pre-cleaned, disposable vials from the HACH company.

7.3 Hot Block, 110°C.

8.0 REAGENTS AND STANDARDS

8.1 Deionized (DI) water: Prepare by passing industrial water through a mixed bed of cation and anion resins. Final DI water has a resistance of 16 MOhms or better. Use DI water for the preparation of all reagents, calibration standards and as the source for dilution water.

8.2 Ammonium molybdate-antimony potassium titrate solution & Ascorbic Acid solution: Purchased as combined color reagent for total phosphorus waters. PhosVer 3 Phosphate reagent: purchased commercially in foil packets for 5-mL sample volume.

8.3 Sulfuric acid (H_2SO_4): Purchased commercially in pre-made 10 mL vials.

8.4 Potassium persulfate: Reagent grade. Purchased commercially in foil packets for 5mL of sample.

8.5 Stock phosphorus solution, 50 mg/L: Dissolve 0.2197 grams NaH_2PO_4 in 1- liter DI water. Solution is stable for 6 months.

8.6 Intermediate phosphorus standard solution: Dilute 20 mL of stock phosphorus solution to 500 mL reagent water; Concentration = 2.00 ppm

8.6.1 Using standard solution (8.5), prepare the following standards in 200-mL volumetric flasks:

mL of Stand. Phos. Soln. (8.5) In 200mL volumetric flask	Conc., mg/L
20mL of a 0.25ppm	0.025
10	0.1

25	0.25
50	0.5
100	1.0
200	2.0

8.7 Sodium hydroxide,1.54 N: purchased commercially.

9.0 PROCEDURE

9.1 Preliminary filtration: Filter samples for determination of dissolved reactive phosphorus, dissolved acid-hydrolyzable phosphorus and total dissolved phosphorus through a 0.45 micron membrane filter. A glass fiber filter can be used for hard-to-filter samples.

9.2 Phosphorus

9.2.1 Add 5 mL of sample and calibration standards to vials which have 2mL H_2SO_4 pre-dispensed into each tube. (Make sure sample is thoroughly homogenized before adding it to the vial).
9.2.2 Add 1 Potassium Persulfate packet to each vial.
9.2.3 Cap and shake each vial vigorously.
9.2.4 Heat the vials in the hot block for 30 minutes at 110°C.
9.2.5 Take the vials out of the hot block and cool for at least 10 minutes.
9.2.6 Add 2 mL of 1.54 N NaOH to each vial.
9.2.7 Add 1 packet of PhosVer 3 Phosphate Reagent to each vial.
9.2.8 Cap and shake the vial vigorously.
9.2.9 Centrifuge the vials that are turbid.
9.2.10 Read each vial at 890 nm using a spectrophotometer using the reagent blank as the reference solution after 5 minutes but no longer than 15 minutes.

10.0 DATA ANALYSIS & CALCULATIONS

10.1 Prepare a standard curve by plotting absorbance against known concentrations of standards. Compute concentration of samples by linear regression. A new calibration curve is analyzed at a minimum of every 6 months or more frequently.

10.2 Obtain concentration value of sample directly from prepared standard curve. Report results as P in µg/L.

10.3 Reagent blanks are not subtracted from samples and should be below the detection limit. Detectable blanks require reanalysis and if still positive, will require either increasing of the detection limit or re-preparation of the sample set.

10.4 Dilute samples if they are more concentrated than the highest standard in the curve. Dilute samples so that they fall between the lowest and highest standard, preferably in the middle of the calibration curve.

10.5 If dilutions are performed, appropriate dilution factors are applied to sample values. The default correction factor for samples prepared using this method is 1.

11.0 QUALITY CONTROL & CORRECTIVE ACTIONS

11.1 Calibration curves are composed of a minimum of a blank and four standards. The correlation coefficient must be 0.995 or greater otherwise re-calibration is performed prior to analysis.

11.2 A laboratory blank is employed at one per sample batch to determine if contamination effects are occurring. A sample batch consists of ≤20 samples. The blank must be below the reporting limit before sample analysis.

11.3 Each matrix has a set of acceptable MS/MSD data for each analytical batch. Prepare one pair of spikes for each 20 samples. Acceptance criteria ±20% or in-house control charts.

11.4 A Second Source Reference check standard is used to verify the calibration and after the analysis of 10 samples as the continuing calibration verification (CCV). This reference check should be within ±10%. If not within the 10%, samples bracketed by the CCVs are reanalyzed.

11.5 A standard is analyzed at the end of the samples and must be within ±10%.

12.0 POLLUTION PREVENTION

12.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

13.0 METHOD REFERENCE

12.1 Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998, American Public Health Association.

14.0 WASTE MANAGEMENT

14.1 Excess Reagents, samples, and method process wastes are characterized and disposed of in an acceptable manner. Phosphorus reagents are disposed of in waste drums. For more information on disposal, see BA013, Sample Disposal Procedure.

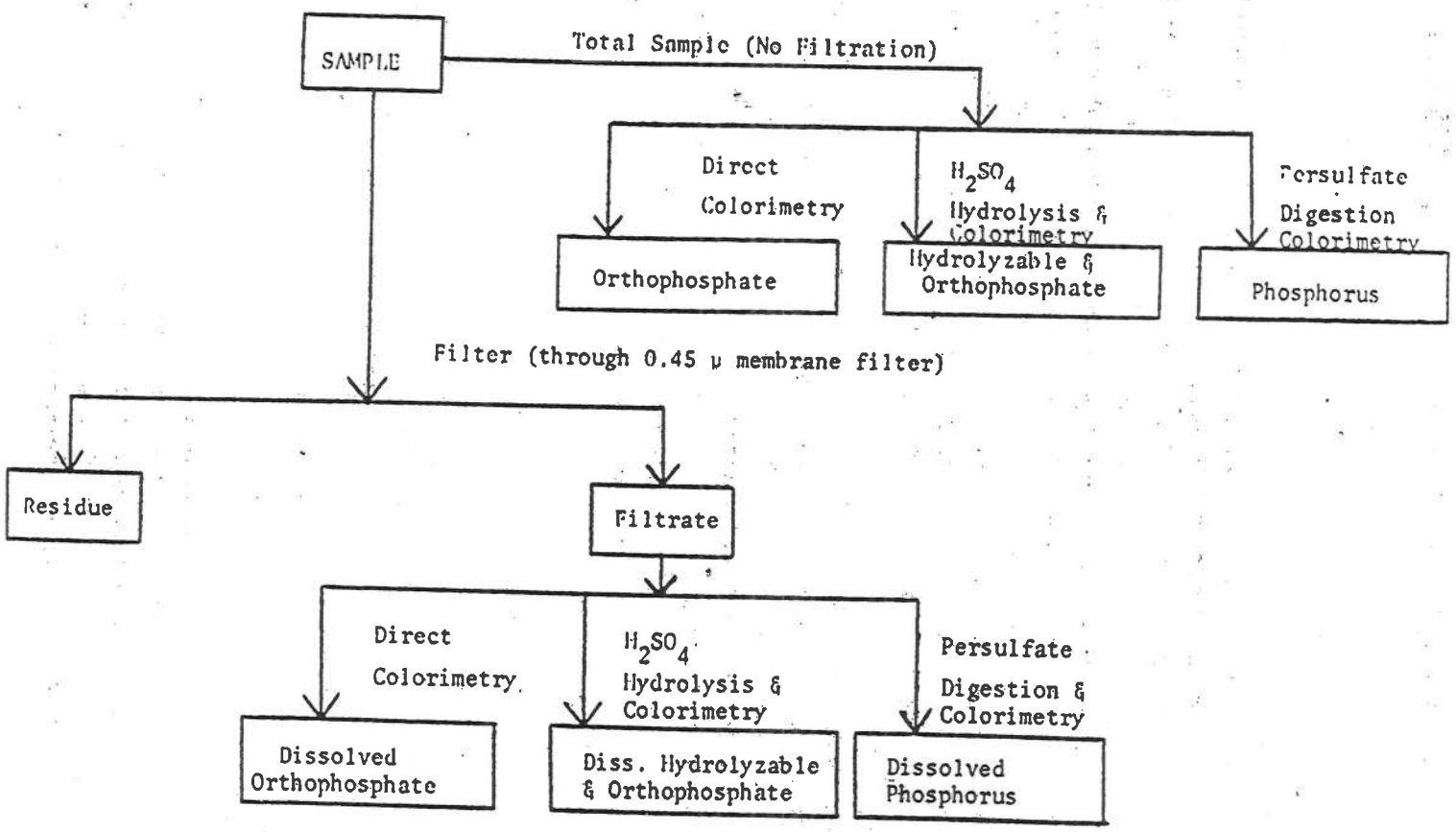

FIGURE 1. ANALYTICAL SCHEME FOR DIFFERENTIATION OF PHOSPHORUS FORMS

Appendix C
Quality Assurance Manual

Brighton Analytical L.L.C.
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QUALITY ASSURANCE PROGRAM PLAN
(QAPP)

For

Brighton Analytical, LLC
2105 Pless Drive
Brighton, Michigan 48114
(810) 229-7575

SOP NO.: BA012

Revision 17

Date Effective: June18, 2014

Michelle M. Meisel
Quality Assurance Manager
Brighton Analytical, LLC

17 June 2014
Date

William J. Topolski
Director of Laboratory Services
Brighton Analytical, LLC

4/16/14
Date

QUALITY ASSURANCE POLICY STATEMENT

This is the comprehensive Quality Assurance Program Plan (QAPP) for Brighton Analytical, LLC. The QAPP outlines the requirements that employees of Brighton Analytical follow to ensure that all the analytical results generated are legally defensible and sound. The object of this manual is to be used as a set of instructions that provide guidance on laboratory policies and their quality control practices in the laboratory. All laboratory employees at Brighton Analytical, LLC are required to follow the procedures set up in this manual to provide high quality analytical data to all clients of Brighton Analytical, LLC.

This document is to be used as a reference document only and is written to maintain laboratory practices that will ensure both the reliability and defensibility of data generated in the laboratory. This manual is intended for use by all personnel at Brighton Analytical, LLC who come in contact with samples and their reported data. Unless otherwise noted, this document is used for all EPA, NPDES, RCRA, Drinking Water analysis, NELAP and non-regulated testing. Brighton Anaytical's laboratory management is committed to compliance with regulatory testing and the TNI Standard.

Brighton Analytical, LLC is dedicated to the continuous improvement in all aspects of our operation and to generate high quality data at all times. The QAPP is continuously being updated for the benefit of the employees and our customers to outline the quality assurance practices that have been developed and implemented.

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FIGURES (Forms)

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DISTRIBUTION OF QA MANUAL

Copy #	Person Responsible

- Master (QA Office) - Michelle Meisel
- 1 Copy Scanned on the copier in the front office

SECTION 1.0 BRIGHTON ANALYTICAL, L.L.C. OVERVIEW

1.1 PURPOSE

The purpose of this Quality Assurance Manual is to provide employees and clients with the overall picture of the laboratory operations at Brighton Analytical, LLC. It is continually updated to provide guidance to the employee of the most current methods and reliable and defensible data to the client. Deviation from the Quality Assurance Manual is only approved by the Quality Assurance Manager and/or Laboratory Director. Brighton Analytical, LLC conducts analysis according to EPA Methodology including: 500 series, 600 series, SW846, Standard Methods, and other approved methods, including methods obtained from the client.

1.2 QUALITY

Brighton Analytical, LLC provides data that is valid, precise, unbiased, scientifically sound, and presented in a timely manner to all clients of the laboratory.

The quality assurance program plan has been set up to meet the objectives of Brighton Analytical, LLC and to follow Good Laboratory Procedures (GLP) as stated in the Code of Federal Regulations. Brighton Analytical's EPA laboratory ID number MI00043.

1.2.1 Brighton Analytical participates in private WP/WS/HW studies on a semi-annual basis. Environmental Resource Associates (ERA) are providers of single blind samples and results are reported to ERA by the laboratory. Results are then reported to the State of Michigan (MI Lab ID#9404) and Louisiana EPA (LELAP Agency Interest No. 176507) via ERA prior to releasing the results to Brighton Analytical, LLC.

1.3 CLIENT CONFIDENTIALITY

Brighton Analytical, LLC is committed to maintaining client information in the strictest of confidence. Information includes, but not limited to, contracts, quotations, correspondence, analytical reports, chains-of-custody, facsimiles, e-mails, analytical work sheets, invoices, raw data, computer disks, samples, and any other information shared with clients. This information will not be divulged to any third party unless required by law or through written authorization by the client or its agent such as an attorney.

1.3.1 Transfer of Ownership/Out-of Business - If Brighton Analytical, LLC ever transfers ownership or ceases operations, each client would be contacted regarding the retention of their data collected. The client would then advise Brighton Analytical, LLC as to the destruction or return of the said data.

1.3.2 Review of Requests, Tenders, and Contracts - The laboratory has established and maintained procedures for the review of request, tenders, and contracts. Requirements, including defined, documented methods and the ability of the laboratory to possess the capability and resources to meet the requirements. A contract can be verbal or written to provide the client with environmental services. For more information, see Brighton Analytical's Standard Operating Procedure, BA020.

1.3.3 Brighton Anaytical affords their clients or their representative's cooperation to clarify the client's request and monitor the laboratory's performance in relation to the work performed. A copy of Brighton Analytical's Sample Acceptance Policy is available for review in sample login and found on the back of all chains of custody. See Appendix D - Brighton Anaytical's Sample Acceptance Policy. It is also displayed in the sample receipt area of the laboratory for review.

1.4 LABORATORY PROCEDURES

The following procedures are conducted and maintained on a daily basis:

1.4.1 Sample Receiving and Storage

1.4.1.1 Each project is assigned a unique project number and each sample is assigned a unique laboratory number. If work must begin before a number can be generated by the computer or sample log-in personnel, the analyst uses the client sample ID. After the sample is logged into the LIMS system and is given a number, the analyst then assigns the number to the work that was completed prior to the number assignment.

1.4.1.2 A Chain-Of-Custody form must accompany samples submitted to the laboratory. COC forms are provided either by the laboratory or the client. Any problems encountered during log-in or sampling may be documented on the form. The original COC is kept with the samples until all analyses are completed. Upon completion, the original COC is sent with the final report to the client. A copy of the COC is kept with the report files at the laboratory and stored for 6 years (files may be kept for a longer period of time upon request by the client). All records including those pertaining to calibration and test equipment, certificates and reports are safely stored, held secure and in confidence to the client. All NELAP-related records are available for review to the accreditating authority.

1.4.1.3 All samples are kept a minimum of 60 calendar days from the date of receipt. Samples may be held longer if requested by the client. Requests are made by facsimile or e-mail. Login personnel mark the samples to identify them for extended hold.

1.4.2 Instrumentation & Maintenance Logbooks

Instrument logs are kept for all instruments to document all routine and non-routine maintenance activities and reference material verifications. The analyst must show the ability to generate acceptable accuracy and precision with each method being performed. Logbooks document maintenance performed (in laboratory by the analyst or service personnel), the instruments overall performance, instrument specific checks and return to control of the instrument.

Records are maintained for each major piece of equipment in the laboratory and all reference materials that pertain to the analytical tests performed. Information in logbooks are to include, but not limited to, name of instrument, the manufacturer's name, type, and identification number including the serial number, date received and date placed into service, current location, condition when received, copy of the manufacturer's instructions, if available, dates and results of calibrations and/or verifications and date of the next calibration and/or verification, details of maintenance carried out to date, and history of any damage, malfunction, modification or repair.

1.4.3 Methodology

The analyst must show the ability to generate acceptable accuracy and precision with each method being performed. Published methods are followed and occasionally Brighton Analytical, LLC will use a method produced by the client. The Laboratory Director, Quality Assurance Manager, or the Department Supervisor must approve all other deviations from actual methods or standard operating procedures.

1.4.3.1 Demonstration of Capability - The laboratory confirms that it can properly operate all methods prior to introducing the environmental tests. If the method changes, the confirmation is repeated. Brighton Analytical completes initial and on-going Demonstration of Capability in water and soil methods to attain accreditation in organic and inorganics. For more information, see Brighton Analytical's SOP #BA023.

1.4.4 Standards & Quantitation

1.4.4.1 Preparation of all standards is documented in a standard logbook found in each department. Standards are analyzed within each analytical batch and/or whatever the method specifies. This includes analyzing continuing calibration checks at a minimum of every 20 samples.

1.4.4.2 Quantitation of each analysis is performed according to method requirements.

1.4.5 Data Review

Laboratory Supervisors' review all data. If the Department Supervisor generates the data then data is reviewed by another analyst or the Laboratory Director. Data is reviewed to ensure that the data was generated and finalized within the method requirements and the laboratory's Quality Assurance Program Plan (QAPP). Data is also reviewed for transcription errors. All reviews are initialed and dated by the reviewer. After review, Data Entry personnel enter the data into the Laboratory Information Management System (LIMS). The final report is reviewed by the Laboratory Director or Quality Assurance Manager for correctness (such as correlation of results for different characteristics of an item) and completeness. The data is signed and dated, copied and sent to the client via fax or e-mail and ultimately mailing the original report with quality control to the client.

1.4.5.1 Nonconforming Analysis - During review, if data is found to be outside the acceptable QC requirements for that analysis, corrective action procedures begin. (For additional information on performing Corrective Actions, see BA SOP #BA010) If data is within the hold time, all samples that are associated with the QC deficiencies must be reanalyzed. If the hold time is past, the client is notified and data qualified on the final report. Corrective actions must take place to find and correct the QC deficiencies. The analyst is responsible for the investigation and documentation of the delinquent quality control.

1.4.6 Data Storage

Raw data is recorded on bench sheets or in bound, paginated laboratory notebooks using permanent ink. Raw data and project files are kept in storage for 10 years. Project files contain complete information of the sample from receipt to reporting of the data within the laboratory minus the raw analytical data and laboratory notebook information.

1.5 QAPP MANAGEMENT

The Quality Assurance Program Plan is reviewed annually by the QA Manager. Revisions take place when changes occur within the laboratory warranting an update to the QAPP. The Laboratory Director and Quality Assurance Manager have the final authorization to make changes to the QAPP. The QAPP is controlled within the laboratory (i.e., red ink stamp) and may be distributed to clients as an "uncontrolled" copy (the red "Controlled Document" will be in black due to copying).

1.6 QA MANAGEMENT PLAN

Brighton Analytical, LLC is dedicated to continually improving all areas of the laboratory's operations to generate high quality data. This QAPP and the Statement of Qualifications (SOQ) are reviewed and/or updated on an annual basis or on an "as needed" basis. Reasons for updating the said plans include, but not limited to, changes in methodology including EPA and MDEQ, changes in daily operations at the laboratory, changes in client requirements/requests, audit responses, etc. Continuous improvement of quality at the laboratory will improve sample throughput which, in turn, will increase profitability.

1.7 RECORD RETENTION

In view of the possible legal use of the data produced, records are maintained a minimum of 6 years (NELAP & Safe Drinking Water Act requirements) unless otherwise requested by the client. Brighton Analytical's computer system is backed up on cassettes on a daily, weekly, monthly, quarterly, and yearly rotation. Data is also backed up on zip drives on an "as needed" basis when the LIMS system reaches capacity. The Laboratory Director stores the records in a separate storage area located at Brighton Analytical, LLC and also is responsible for monitoring the records.

1.7.1 The records room (long-term storage) is monitored by an access log. Storage and access to the records is documented by a log that monitors the removal/return of records from the room by date, initials, and time removed/returned. The access log is monitored by the Quality Assurance Manager.

SECTION 2.0 LABORATORY FACILITY, ORGANIZATION & EQUIPMENT

2.1 INTRODUCTION

Brighton Analytical, LLC began operations in April 1986 offering various chemical analyses of environmental samples. The goal is to offer the highest quality analytical services to our customers with a prompt sample turn-around-time of no more than 10 working days. Present capabilities include analysis of drinking water, ground water, wastewater, soil, oil, air (including tubes, filters and tedlar bags), and various other media, all referencing EPA test method protocols. (See Appendix A – List of Most Commonly Requested Methods).

Brighton Analytical, LLC is a small, privately owned business that staffs 12 full-time employees. The staff includes nine degreed Chemists and the remaining technical and administrative support. Corporately, Brighton Analytical, LLC has over 20 years experience in the testing of U.S. EPA Methods, ASTM Methods and Standard Methods.

2.2 FACILITY

2.2.1 Brighton Analytical, LLC occupies 12,000 ft^2 of laboratory space. The building contains separate instrumentation labs including a positive-pressure volatile instrumentation lab, an isolated extraction laboratory, sample preparation lab, a low level mercury lab, three walk-in refrigerated storage areas, seven offices, a computer room, and a shipping and receiving area. The environmental conditions (temperature, humidity, etc.) and energy sources (lighting) are monitored in the laboratory to ensure that the instruments are operating within recommended manufacturers instrument ranges. Temperature is set within operational range of the laboratory instruments. All refrigerators and coolers are monitored/recorded daily to ensure proper temperature of samples, standards, extracts, etc. Attention is paid to biological sterility, dust, electromagnetic disturbances, humidity, electrical supply, temperature, and sound and vibration levels. If any of these occur, information is documented in each instruments preventative maintenance/function verification logbook that is effected. Testing is stopped if environmental conditions jeopardize the results of the tests.

2.2.2 Laboratory operations include organic and inorganic analysis. The organic section includes analysis consisting of extraction, gas chromatography, infrared spectroscopy, and gas chromatography/mass spectrometry. The inorganic section includes wet chemistry, ion chromatography, gravimetric analysis, and inductively coupled plasma (ICP) including mass spectrometry.

2.3 PERSONNEL QUALIFICATIONS

Brighton Analytical, LLC staffs 12 full-time employees. (See Figure 1.0 - Internal Organizational Chart). The laboratory is, and remains, impartial and all Brighton Analytical employees are free from any undue commercial, financial, or other pressures which might influence their technical judgement. The following is a list of positions within the laboratory:

2.3.1 Director, Laboratory Services

The responsibility of the laboratory director is to assure that all activities are performed according to methods and protocols specified in the QAPP. The Laboratory Director also oversees and supervises the employees and day-to-day operations of the laboratory, ensuring that programs are in place and evaluating and implementing changes in methodology and quality control measures. The Director may recommend, discipline, suspend, or terminate employees for noncompliance or repeated noncompliance with established policies or procedures; or for dishonesty in representing that they have complied with policies or procedures at any time.

The laboratory director is ultimately responsible for ensuring that all laboratory personnel have demonstrated proficiency for their assigned functions and that all data reported by the laboratory meet the required quality assurance criteria and regulatory requirements.

The Laboratory Director may also handle client complaints, personnel training, quality assurance compliance and sufficient staff and equipment available to complete all tasks and perform analyses within the established time frames. The Laboratory Director reviews and signs all final reports before they are submitted to the client.

2.3.2 Manager, Quality Assurance (Technical Director)

The Quality Assurance Manager requires a minimum of a bachelor's degree in science and at least four years experience in an environmental laboratory. The QAM should also belong to at least one professional affiliation. The QAM has a working knowledge of the statistics involved in quality control of laboratory analysis and basic understanding of the methods in which the laboratory employs.

The QAM is responsible for the development and implementation of the quality assurance plans within the laboratory. The QAM also approves and monitors corrective actions to resolve non-compliance within the laboratory. The QAM reports directly to the Laboratory Director. The QAM may also handle client complaints, personnel training and reporting to the Director on activities such as corrective actions, client quality complaints, quality procedures and quality problems. The QAM is able to evaluate data objectively and perform assessments without outside influence such as managerial. They also have a general knowledge of the analytical test methods being performed for which data review is performed.

The QAM serves as a focal point for the quality control issues in the laboratory and functions independent from daily laboratory operations. The QAM has documented training and/or experience in QA/QC procedures and is knowledgeable in the quality systems defined in the NELAC (TNI) standard.

The QAM may serve as a backup to the Laboratory Director if needed in final report review and release. Only the QAM and Laboratory Director have authorization to release any final reports to the client.

The QAM is also the acting Technical Director. The technical director certifies that all personnel with appropriate educational and/or technical background perform tests for which the laboratory is accredited under NELAC. Documentation is kept in the training files on each analyst. Training files are located in the Quality Assurance Office.

2.3.3 Customer Service Manager

The Customer Service Manager is responsible for customer service activities. Responsibilities include the administration of business including personnel, purchasing, marketing, and controller. The Customer Service Manager also handles client complaints and complaint follow-up.

2.3.4 Department Supervisor

The Department Supervisor should have at least a bachelor's degree with a major in chemistry or equivalent and at least two years of environmental laboratory experience. The Department Supervisor should have a working knowledge of quality assurance principles and be responsible to ensure that all laboratory personnel have demonstrated the ability to satisfactorily perform the analyses to which they are assigned. The Supervisor also ensures that all data reported by the laboratory meets the required quality assurance and regulatory criteria.

The Department Supervisor has many duties which may include, but not limited to, personnel work assignments including the coordination of work so all tasks are completed within established time frames, monitoring of backlogs, preparation of SOPs, training of personnel, overseeing preventative maintenance activities, and instrument purchasing.

Supervisors ensure that all activities are performed according to methods and protocol specified in the SOPs. They may recommend changes in standard operating procedures and quality control measures to the Laboratory Director.

The Supervisors also assume the responsibility for reviewing departmental work and assuring that outputs are accurate before release of departmental data. They also perform analyses on a daily basis. Supervisors require that all employees in the area under their supervision adhere to this QAPP.

2.3.5 Analyst

The laboratory analyst requires a minimum of a bachelor's degree with a major in chemistry or equivalent and at least one year of experience in the analysis of environmental samples. The bachelor's degree requirement may be waived when years of experience are taken into consideration. Data produced by analysts and instrument operators while in the process of training and gaining experience are acceptable only when reviewed and validated by a fully qualified analyst or the laboratory department supervisor.

The analyst is responsible for calibrating the instrumentation, performing daily, weekly, monthly and yearly maintenance, troubleshooting instrument problems, ordering parts, and service requests. The analyst is also responsible for generating valid, representative, quality data in a timely manner. The analyst follows various published methods and standard operating procedures (SOPs) including the required department QC for the method being followed. The analyst reports directly to the department supervisor regarding instrument problems and turnaround times.

2.3.6 Technician

The laboratory technician should have at least a high school diploma or equivalent. If the technician is to analyze samples, he or she should complete a method-training program under an experienced analyst and have six months bench experience in the analysis of environmental samples. Responsibilities of a Technician include sample preparation, glassware cleaning, laboratory cleaning, bottle preparation, and assisting chemists in sample loading and general preparation.

2.3.7 Sample/Data Control

Responsibilities include receiving and logging in samples to the LIMS system, data entry and reporting, assuring chain-of-custody on all samples, identifying special requests and advising chemists accordingly.

NOTE: **Academic Training** - The Laboratory Director may waive the need for specified academic training, on a case-by-case basis, for highly experienced analysts.

2.4 EMPLOYEE RESPONSIBILITIES

Each employee at Brighton Analytical has a personal stake in the quality of the laboratory's work generated. It is the responsibility of each employee to implement the quality assurance programs according to their assigned duties.

2.4.1 Each employee at Brighton Analytical, LLC has the following quality-related functions:

2.4.1.1 Complying with this QAPP and all applicable methods, SOPs, and other required documentation at all times. Each employee must review pertinent SOPs and the QAPP annually and sign a release stating that they have read, understood, and will implement the information provided in the quality manual and SOPs.

2.4.1.2 Ensuring that the quality of all the data generated meets the required level of quality before releasing it. Although all employees work is inspected, each employee remains fully responsible for the quality of his or her work. An employee may not rely on later reviews of their work to catch errors. Results must meet all applicable quality requirements before it is released.

2.4.1.3 Each employee undergoes data integrity training/ethics training on an annual basis. This is documented in the training files. The signature page also serves as a log of names, initials and signatures for all individuals in the laboratory responsible for signing or initialing any laboratory record.

2.5 EQUIPMENT AND CALIBRATIONS

Any equipment or methodology that can influence a measured value is calibrated to the accuracy requirements for its intended use. Reference standards of measurement are calibrated according to traceability to national/international standard reference materials. If a piece of equipment is not operating within its limits, the instrument is labeled with a "NOT IN SERVICE" sign and implementation of the corrective action necessary to bring the equipment back into control will be documented in the maintenance logbook for the particular instrument.

All equipment is verified before being put into service and also on a continuing basis. All equipment is calibrated according to the methodology being cited. Equipment used in environmental testing is calibrated and verified using source reference material which is traceable to the Certificate of Analysis. All measurements made are traceable to national standards of measurement.

2.5.1 Balances

All balances (top loaders and analytical) are checked against Class 1, NIST traceable weights daily or when used. (See Table 1.0 - Inventory of Balances). All balances are calibrated monthly by the QA Manager in which three weights are used to bracket the working range of the balance. Balances are calibrated annually from an outside source. All annual and monthly balance calibration information can be located in the Quality Assurance office. Daily balance calibration is located next to each individual balance.

Class 1 NIST traceable weights are calibrated every 5 years by an outside source. If the daily balance check is not within requirements (calibration ranges are found on each of the daily log sheets), a "Not in Service" sign is immediately placed on the balance and the QA Manager is notified. The QA Manager will arrange service for the balance. All information to get the balance back into service is recorded on the daily bench sheet. (See Figure 2.0 - Daily Balance Record)

2.5.2 Thermometers

All thermometers are calibrated against a NIST-certified thermometer. Thermometers purchased as (non)-NIST-certified must be validated in-house before placed into use and verified annually thereafter. (See Table 2.0 – Thermometer Inventory)

Thermometers in Microbiology All coolers/refrigerators that contain samples and standards are replaced or calibrated annually with NIST certified thermometers, including the autoclave. Thermometers in Microbiology are calibrated on a semi-annual basis. If purchased, the certificate is located with each thermometer in the designated areas.

Thermometers that are calibrated in-house are calibrated within its working range of use. The point must fall between $\pm$ 2°C for the thermometer to be acceptable. If the thermometer fails the criteria, it is re-calibrated a second time. If it fails again, the thermometer is discarded and replaced with a new one. A sticker containing the NIST certified correction factor (obtained during calibration), calibration expiration date and thermometer ID is placed on the in-house calibrated thermometers.

2.5.3 Refrigerators and Freezers

A refrigerator/freezer inventory can be found in Table 3.0. Refrigerators and freezers are checked daily to ensure proper performance against the limits defined below:

- Refrigerators : 4°C (acceptable working range: 2°C to (<)6°C)
- Freezers: -15°C (acceptable working range: -10°C to -20°C)
- Ovens: acceptable working range: $\pm$ 2°C at operating temperature

Temperatures are recorded daily by assigned personnel. The actual temperature of the unit and the correction factor are both recorded. The form for recording temperatures is found in Figure 3.0. If any of the above fail to meet the criteria stated, the QA Manager is notified immediately. Corrective actions are

initiated to locate and correct the problem. If the sample walk-in coolers do not meet the specified criteria, a service person is called immediately to fix the problem. If the service person is unable to make it to the laboratory the same day, samples are removed from the cooler that is not meeting specifications and placed in a different cooler until the problem is fixed. This information is documented on the daily temperature form that is attached to each refrigerator/freezer.

2.5.4 Incubators – BOD and Microbiology

There are three incubators within the laboratory. The BOD incubator is maintained at 20°C with an acceptable working range of 19°C to 21°C. The two microbiology incubators are kept at 35°C with an acceptable working range of 34.5°C to 35.5°C. The BOD thermometer is replaced or calibrated annually against NIST-certified thermometers and the incubator thermometers are replaced or calibrated semi-annually against NIST-certified thermometer.

2.5.5 Pipettes

Pipettes are calibrated on a quarterly basis. Mercury pipettes are documented in the instrument logbook. All other calibrations are found in the metals laboratory. If a pipette does not meet calibration criteria, ±2% of the pipette's capacity, it is re-calibrated. If calibration fails a second time, the pipette is discarded and replaced. The Quality Assurance Manager and analyst are notified immediately of any failure.

2.5.6 Syringes

Hamilton (gas-tight and non-gas tight) are manufactured to be accurate within ±1% of total syringe volume. The accuracy and precision Statement of Conformance can be found in the Quality Assurance Office.

2.5.7 Microwave Digestor

Calibration of Microwave Equipment - Brighton Analytical's microwave unit uses temperature feedback control capable of replicating the performance specifications of the method, therefore, the calibration procedure may be omitted. The temperature is checked and verified on a quarterly basis with a NIST traceable thermometer and recorded in a logbook. If microwave does not meet the temperature required, a "Not in Service" sign is placed on it and a service call is made. The sign remains on the digestor until the instrument is back into control.

SECTION 3.0 TRAINING

3.1 NEW HIRES

All new hires must go through a training period. This amount of time is based on prior experience and job performance. Laboratory Supervisors or qualified analysts may perform the training. The new employee must demonstrate competency before analyzing client samples. The new employee is required to read the relevant SOPs according to the job to be performed and sign off that they understand the procedures. The department supervisor decides when the new hire is ready to analyze client samples. Each employee may receive training from different departments within Brighton Analytical and also from external sources. New hires also must read the Quality Assurance Program Plan before beginning any analysis. The employee also signs an agreement that they have read, understood, and will follow the procedures listed in the QAPP.

3.2 TRAINING ASSESSMENT

Each employee is adequately trained to perform their assigned tasks. Employees' training and qualifications to perform their appointed tasks are documented. Initial demonstration of capability is completed each time there is a change in equipment, personnel, or test method.

3.3 PROCEDURAL TRAINING

3.3.1 The first step of the training process includes the familiarization of all the pertinent SOPs in-house. These SOPs will be supplied to the employee. Each SOP should include a section that details the procedure, a section that lays out the documentation that is required, and a section that lists the specific quality required. The employee reviews the SOPs and the trainer/instructor answers any questions that the employee may have. The employee then signs off that they have read, understand, and agree to the standard operating procedure. This is placed in the employees training file.

3.3.2 The process is then described in detail to the trainee and demonstrated. The trainee repeats the above process as the instructor observes for error.

3.3.3 Once the new employee has completed instruction, and has read and understands each applicable SOP documenting the process, they must demonstrate proficiency. In the case of a laboratory analysis procedure, this requires the person to successfully analyze a sample "blind" and/or demonstrate acceptable precision and accuracy.

3.4 ANNUAL TRAINING (Data Integrity/Ethics/ MDLs)

3.4.1 All analysts participate in a semi-annual blind for wastewater, potable water and soil at the laboratory. Annually, each employee reads the Quality Assurance Program Plan and signs off on a form that they have read, understood, and agree to the procedures in the QAPP. This is added to their training file.

3.4.2 A method detection limit is performed annually and placed in the employees training file. Additional information on performing MDL studies can be found in BA SOP #BA003.

3.4.3 Each employee is required to participate in data integrity/ethics training. Attendance is taken and added to each employee's training file. Discovery of potential issues are handled in a confidential manner to assure confidentiality and a receptive environment in which all employees may privately discuss ethical issues or report items of concern. In no ways are employees subject to retaliation for reporting data integrity issues. In instances of ethical concern, the mechanism includes a process whereby laboratory management are informed of the need for any further detailed investigations. All findings of inappropriate activity are documented including disciplinary actions taken. All documentation of these issues is kept for a minimum of 5 years. Additional information including the procedure for data integrity training/ethics training can be found in BA SOP #BA019, Data Integrity Training (Ethics Training).

3.5 WRITTEN HAZARD COMMUNICATION PROGRAM

A hazard communication program has been set up at Brighton Analytical to ensure the health and safety of its employees. The hazard communication program provides information about the hazardous materials present in the laboratory. (See SOP #BA014 for more information)

SECTION 4.0 SAMPLE CUSTODY

4.1 GENERAL REQUIREMENTS

4.1.1 Log-In Personnel at Brighton Analytical are responsible for inspection, documentation, and log-in of all samples received at the laboratory. The lab will continue to maintain the chain-of-custody procedures until the analyses are completed and the samples are disposed. (See Figure 4.0 – Brighton Analytical's Chain-Of-Custody Form)

4.1.2 Any problems occurring during sample receipt and check-in are noted on the COC such as inappropriate bottle types or sample preservation. All information including sample identification, time and date of collection, sample matrix, bottles and preservation, collector's name and date of sample receipt is included on the COC.

4.1.3 The chain-of-custody (COC) form is reviewed annually and updated if necessary.

4.2 SAMPLE RECEIPT AND LOG-IN

4.2.1 Upon receipt, the lab records information on the COC documenting the condition of the samples upon arrival. The temperature of the samples are taken and recorded on the chain-of-custody form (except samples for metal analysis). If samples were collected and delivered to the lab on ice but have not achieved a 4°C (2°C to 6°C temperature range), the login personnel note "received on ice" on the COC and the temperature of the sample(s). For certified drinking water analyses only, login personnel ask if the sample is from a chlorinated water supply. If it is, analysts in the volatile department are notified. Final data reported to the client must be footnoted: Chlorine not neutralized by ascorbic acid and trihalomethanes may be affected/elevated. The client may also be asked if the pH is >10 or <2. The pH is taken on all samples except for volatile analysis, in which, the pH is taken after analysis is complete.

4.2.1.1 Samples that do not meet shipping, holding time, and/or preservation requirements are immediately placed on hold until the client can be contacted. Samples requiring preservation that are received unpreserved are flagged on the COC, preserved in login, and data qualified on final report. All faxes that are received or sent by the client are retained as permanent record. If analysis proceeds on the above-mentioned samples, the compromised samples are noted on the final report to the client.

4.2.1.2 If volatile drinking water samples are <u>not</u> preserved, they have a 24-hour holding time. Collection date/preservative are noted on the COC.

4.2.1.3 Sodium thiosulfate is provided to the client in sterile sample bottles for microbiological analysis in case the source is a chlorinated water supply. This binds to any chlorine in the sample, that may not have been flushed out, to prevent a false negative.

4.2.1.4 Microbiology samples received at the laboratory frozen or high in chlorine are rejected.

4.2.2 Each sample is assigned a unique laboratory number. The laboratory ID number is placed on the sample container (top and side) as a durable, water-resistant label.

4.2.3 Sample information is recorded into a permanently bound logbook. The notebook is recorded in the Laboratory Notebook Record of Issue. The information includes the Brighton Analytical project number, date received, client/project name/project number, matrix, date sampled, client sample ID, person responsible for logging into the book, and the laboratory ID#. The date the samples were disposed of is added at a later date. If the sample has a "Rush" turnaround time or special QC requirements, the sample is highlighted in the logbook. If the client requests an out dated method, they are notified by phone or facsimile. The client may then change the method to the laboratory only in writing.

4.2.3.1 If samples are deemed hazardous via the analytical process, they are noted in the computer when analytical results are entered. A list of hazardous samples is generated by data entry personnel on an as-needed basis when samples are being disposed of. (See Table 4.0 – Hazardous Waste Disposal Criteria)

4.2.4 Sample information is then entered into the Laboratory Information Management System (LIMS). The laboratory sample ID number serves as a link to all laboratory activities associated with that sample including preparation, analysis, standards, etc. Problems encountered during sample receipt (i.e., received past hold time, inappropriate containers or preservation, insufficient sample volume, out dated methods, etc.) are added as comments to the system at this time. The comments are reflected on the final report.

4.2.5 Paperwork is generated for each department to provide information on the pending analysis, sample matrix, date sampled, and sample due date. There is also space for the analyst to write the final results on after analysis is complete. Special turnaround times or quality report requirements are identified on this sheet. Any problems noted with the samples during receipt or special procedures required for analysis are also placed on the analyst's paperwork and raw data.

4.2.6 A Project Modification Report is initiated anytime a change to the project is requested by the client, but a facsimile or e-mail is still pending. The changes may include, but not limited to, adding/deleting analysis, change of due date, project cancellation, re-prepping/re-analyzing samples, method changes or taking samples off hold. (See Figure 5.0 – Project Modification Report)

4.2.6.1 Changes made to a project may be initiated verbally by the client, but a hardcopy notification either by fax, letter, or e-mail must accompany the request. This change will be filed with the original COC for documentation.

4.2.7 If necessary, Brighton Anaytical, LLC submits any subcontracted work for testing covered under NELAP only to a laboratory accredited under NELAP for the tests to be performed or one that meets applicable statutory and regulatory requirements for perfoming the tests and submitting the results of tests performed.

4.3 SAMPLE AND LIMS SECURITY

Brighton Analytical, LLC is a limited access facility. All visitors must go through the reception area upon arrival at the laboratory. A Brighton Analytical employee accompanies visitors at all times.

The LIMS system is user name and password protected. Only authorized personnel can access the LIMS which is limited to Data Entry Personnel, the Laboratory Director, and Quality Assurance Manager. Instrument data systems are also password protected. Only authorized personnel have access to the systems. The LIMS system and data systems are set up with audit trails. All activity performed on the systems are recorded and can be accessed only by authorized personnel.

4.4 SAMPLE DISTRIBUTION, TRACKING, AND REPORT GENERATION

4.4.1 Samples are received daily via Federal Express, UPS, USPS or DHL. After log-in, the samples are placed into a 4°C (±2°C) cooler until analysis. Samples are stored away from all standards, reagents, food and other potentially contaminating sources including highly contaminated samples. Highly contaminated samples are stored in a temperature-controlled environment away from the other samples to prevent cross contamination, usually in Zip-lock bags for protection. Highly contaminated samples requiring volatile analysis are stored in their own temperature-controlled cooler away from the other volatile samples (See Table 3.0- Refrigerator/Freezer Inventory). After samples are analyzed, the analyst performs a sample write-up, data is reviewed and entered into the LIMS by data entry personnel and a final report is generated.

4.4.2 Final reports go through one last review for completeness. The reviewer checks the analysts' worksheet against the final report for errors. If no errors are detected then the results are dated and initialed by the reviewer and sent to the client. If an error is detected, the raw data is reviewed, changes are made if necessary, and then a new final report is generated. This procedure is to eliminate transcription errors.

The record keeping system allows the historical reconstruction of all laboratory activities that produced the analytical data, including the identity of personnel involved in sampling, preparation, and testing of the samples. History of the sample may be readily understood through the documentation.

NOTE: For a more detailed instruction on sample control, see Brighton Analytical SOP #BA002. For more detailed information on report generation including data review, see Brighton Analytical SOP# BA021.

SECTION 5.0 INSTRUMENTATION, SOFTWARE & SUPPLIES

5.1 INSTRUMENTATION & SOFTWARE

A current list of instrumentation in the laboratory is kept by the QAM. The list can be found in the laboratory's Statement of Qualifications and this Quality Assurance Program Plan. Analysts are responsible for preventative maintenance and ordering supplies, including standards and instrument parts, for each analysis performed. (See Table 5.0 - Laboratory Instrument

Inventory). Instruments that are currently not working or being serviced are labeled "Not-In-Service" until at which time the instrument is up and running and the sign is removed.

5.1.1 Instrument Verification - Before being placed into service, instruments are calibrated or checked to establish that they meet the laboratory's specification requirements. The analyst either analyzes a performance evaluation test or a certified reference standard to confirm the instrument is ready for use. A calibration curve is analyzed according to the specific method and a method detection limit is performed. Pending acceptable results to all these, the instrument is then placed into use. Instrument data systems are password protected. Only authorized personnel have access to the systems.

5.1.2 Software Verification - All computer software prior to use is validated and controlled by the analyst and the software installer. Brighton Analytical retains computer technical support personnel to ensure that procedures are established for data entry integrity, data storage and data transmission. Computer and automated equipment is maintained to ensure proper functioning and provided with the environmental and operating conditions necessary to maintain the integrity of calibration and test data. Commercial, off the shelf software, is also documented that it is validated before being put into use. The only program in the laboratory that performs calculations directly from the raw data is the ICP/MS data software. This software was originally installed by the instrument manufacturer and validated. The program is locked and protected from any outside manipulations. The only person able to make changes to the program is a licensed software programmer.

5.2 LOGBOOKS

5.2.1 Run logs are retained for each instrument, standard preparation and maintenance of all instruments in the laboratory. Each instrument has its own maintenance and run log. Instrument logs can be found next to each instrument.

5.2.2 Logs are maintained for daily refrigeration/freezer check, incubator & autoclave check, daily balance check, and daily conductivity check on the DI water system. This data is filed on an annual basis in the Quality Assurance Office.

5.2.3 For Microbiology, permanent records are recorded for commercially prepared media. Information includes, but not limited to, date received, types of medium, lot number and pH verification. Records are also kept on the ColiSure medium. Each new lot of media is checked for autofluorescence and recorded.

5.2.4 For additional information of the control and issuing of logbooks, see Brighton Analytical SOP #BA011.

5.3 INSTRUMENT MAINTENANCE LOGS

5.3.1 Logbooks are kept for each instrument to document preventative maintenance and repair. All service to the instrument should be recorded in the logbook including cleaning, outside service calls, new calibrations, changes made to the instrument that would change performance such as baseline, threshold, etc., and how the instrument is performing overall.

5.3.2 Some aspects of maintenance will be initiated as performance causes the measurements to be outside of the control limits. Other maintenance is performed on a continuous basis and is considered preventative maintenance. Information that is documented daily by the analyst in the maintenance log may include, but not limited to:

- Overall performance of the instrument.
- What maintenance, if any, was performed.
- What repairs, if any, were performed.
- Any additional information that may be pertinent for future reference.
- Instrument specific checks that have been done.
- Return to control if maintenance was performed at an earlier date.

5.3.4 For microbiology, record information such as quarterly checks on the autoclave's automatic timing mechanism and the temperature of each autoclave cycle to ensure that sterilization is adequately achieved. The length of the autoclave cycle (a minimum of 30 minutes at 121°C is required before disposing contaminated test materials.

5.3.5 Each logbook contains the instruments operating conditions. This may also be included in the method specific SOP but is readily updated in the instrument logbook.

5.4 SUPPLIES

Supplies are available for all analysis being performed within the laboratory. Routine maintenance (expendable) supplies are available at all times. If instrument problems arise, the analyst is responsible for sufficient supplies to be available to fix the instrument. The analyst is also responsible for ordering and storage of all standards and consumable materials necessary to complete analytical tests. An order form is placed in the main hall of the laboratory. The analyst writes the information for the supply needed on the form and the Laboratory Director places daily orders. If the analyst needs the supplies immediately, they may order themselves. A list of suppliers is available in the purchase order book located in the lunchroom.

5.5 GLASSWARE

Glassware is used on a daily basis within the laboratory. Borosilicate glass is the most commonly used glassware for sample preparation. Brighton Analytical purchases all of its containers for sample collection as pre-cleaned containers. Sample containers are used one time and then discarded.

5.5.1 Volumetric Glassware

Volumetric glassware is etched on the side of the device indicating the temperature at the time of calibration. If there is not a temperature, the 20°C can be assumed as the standard. Reagent and calibration solutions should always be dispensed at the same temperature at which they are prepared. Volumetric pipettes are usually marked with a TC (to contain) or TD (to deliver). The analyst should decide which one is best suited for the measurement being performed.

Class A volumetric glassware is etched on the side with an "A" by the manufacturer. Class A glassware does not need to be calibrated before use.

Volumetric glassware is always air-dried. It is never heated after it is cleaned. Heating the volumetric glassware will cause the glass to expand and contract, therefore, compromising the accuracy of the measuring device.

5.5.2 Glassware Cleaning

5.5.2.1 Brighton Analytical purchases pre-cleaned glassware for sample collection. All glassware used in sample collection is discarded after one use.

5.5.2.2 Glassware used in the analysis procedure is cleaned according to the type of test it is to be used for. For cyanide, phosphate, mercury, metals, organics, and miscellaneous glassware, see Brighton Analytical's SOP #BA005 for complete information on how to clean the laboratory glassware.

5.6 REAGENTS AND SOLVENTS

5.6.1 Definition

Reagents and solvents are any chemical substances used to dissolve, digest, extract, react, or interact with any sample or analytical component of the sample. The grade of reagents and solvents used in the laboratory are equal to, or greater than, what is noted in the approved method and Brighton Analytical's SOPs. The reagents and solvents are purchased from commercially available sources. All reagents are marked with the date of receipt, date opened, storage requirements, expiration date and verified by the analyst of purity.

5.6.2 Reagent Shelf-life

Reagent shelf life is strictly observed. In general, purchased reagents will not be kept longer than their labeled expiration date. If an expiration date is not provided by the manufacturer, solids and neat reagents are kept for up to ten years and solutions kept for up to two years from date of receipt.

5.6.3 Storage of Solutions

At a minimum, dilutions of purchased solutions or solutions prepared from solid reagents/neat reagents will be clearly labeled with those items below:

- Reagent or Standard name and/or Formula.
- Concentration of reagent or standard.
- Date of preparation and expiration.
- Initials of person that prepared the solution.
- Storage requirements.

5.7 STANDARD SOLUTIONS

Documentation of all standards is maintained within each section of the laboratory. Each standard that is prepared is given a unique number so that it can be traced throughout the analysis procedure. Documentation includes, but not limited to, manufacturer/vendor, manufacturer's Certificate of Analysis, date of receipt, storage conditions, and expiration date of the standard. (See Figure 6.0 - Standard Preparation Log Page).

5.7.1 Original standard containers are labeled with the date received, date opened, expiration date and the analyst's initials.

5.7.2 All calibration standards are verified within $\pm$10% against a second source.

5.7.3 Standard solutions are replaced within the holding times of each type of analysis or verified against fresh standards. (See Table 6.0 for holding times of standards and reagents used in the laboratory)

5.8 DISPOSAL

Safe disposal practices are followed at Brighton Analytical, LLC. Hazardous chemical waste is properly segregated and disposed of by a licensed hazardous waste-hauler. Analysts are trained in the identification of hazardous and non-hazardous waste. Standards are considered hazardous waste and caution is used in their use and disposal. (See Brighton Analytical's SOP #BA013 – Sample Disposal Procedure)

Environmental test samples that are classified as hazardous waste according to Brighton Analytical's Sample Disposal Procedure will be returned to the customer or disposed of through a licensed hazardous waste-hauler. Sample disposal is in accordance with state and federal regulations.

SECTION 6.0 FIELD SAMPLING AND SUPPLIES

6.1 SAMPLING PROCEDURES

6.1.1 **Sample Collection** – Samples are collected following the published methods within the EPA protocol including correct preservative, sample containers, and sampling technique. For microbiological sample collection, the sample collector should be trained in aseptic sampling procedures and, if required, approved by the appropriate regulatory authority or its designated representative (See Appendix B – Microbiological Sample Instructions).

6.1.1.1 Microbiology – (drinking water samples) Samples must be representative of the water distribution system. Water taps used for sampling should be free of aerators, strainers, hose attachments, mixing type faucets, and purification devices. Cold water taps should be used. The service line must be cleared before

sampling by maintaining a steady water flow for at least two minutes (or until the water changes temperature). The container is filled to the line marked on the bottle when collecting the sample. (See Appendix B for Microbiological Sampling Guidelines). Immediately after collection, a chain-of-custody is completed containing the following information:

- Name of system (public water system site identification number, if available).
- Sample identification (if any).
- Sample site location.
- Sample type (e.g., routine distribution system sample, repeat sample, raw or process water, other special purpose sample).
- Date and time of collection.
- Analysis required.
- Disinfectant residual.
- Name of sampler and organization (if not the water system).
- Sampler's initials.
- Person(s) transporting the samples from the system to the laboratory (if not the sampler).
- Transportation condition (e.g., <10°C, protection from sunlight). If a commercial shipper was used, shipping records should be available.
- Any remarks.

6.1.1.2 Microbiology – (Source water samples) Samples must be representative of the source of supply, collected not too far from the point of intake, but at a reasonable distance from the bank or shore. The sample volume should be sufficient to perform all the tests required.

6.1.2 **ISCO Auto-sampler** - Brighton Analytical provides an ISCO auto-sampler to the client for water field sampling. The client may collect the sample or request an employee of Brighton Analytical to perform the sampling. In either case, appropriate sample bottles and preservatives are provided to the client by Brighton Analytical per NPDES requirements.

6.1.3 **Analytical Results Limitations Due to Matrix** - Any limitations on the analytical results or the sampling procedures due to the sample matrix will be specified to the customer in the final report.

6.1.3.1 The acquisition of the above information may come from the client before the samples are logged in or as a result of the analysis. This information is documented on the COC or on the raw data by the analyst.

6.1.3.2 It is the responsibility of the Log-in clerk to ensure that all documented discrepancies are noted on the chain-of-custody.

6.2 SAMPLING BOTTLES AND PRESERVATION

6.2.1 Requirements

Individual bottles will be prepared or purchased according to the specifications of their end use. Sample bottles will meet the requirements for cleaning, labeling, and chemical preservatives, when necessary, as defined below:

- Primary Drinking Water contaminants- (Code of Federal Regulations) – 40 CFR 141.1-141.30.
- Secondary Drinking Water contaminants- 40 CFR 143.1-143.5.
- NPDES- 40 CFR 136.
- RCRA – SW846: Chapter 2, Revision 1, July 1992.
  Chapter 3, Revision 3, December 1996.
  Chapter 4, Revision 3, December 1996.

6.2.2 Trip blanks

Trip blanks for volatile organic analyses are included with each set of VOA bottles sent out for sampling. Coolers and cold packs/ice are also provided upon request.

6.2.3 Labeling Bottles

Labels are placed on bottles before going to the client. The label is stamped with the type of preservative, if any, found in the container.

6.3 COMPOSITING SAMPLES

Clients may composite samples or samples may require composite in the laboratory. Samples are composited by an analyst in the laboratory. Follow Brighton Analytical's SOP procedure on compositing samples, SOP #BA015 for more information.

6.4 CONTAINERS, SAMPLE PRESERVATION AND HOLDING TIMES

6.4.1 Individual bottles are prepared or purchased according to the specifications of their end use. Samples must include the appropriate preservative and be labeled on the outside of the container. If no preservative is indicated, log-in personnel must acquire the necessary information from the client and preserve the sample if applicable. (See Table 7.0 & 8.0– Containers, Preservation Techniques, and Holding Times for Aqueous and Solid Matrices). For more detailed guidelines on sampling for environmental samples, see Appendix E. Samples can be preserved in login if sampled the same day.

6.5 SAMPLES TRANSPORTED TO THE LABORATORY

6.5.1 Sample Icing - Client should keep samples (except samples that require only metal analyses) at 4°C during transit to the laboratory.

6.5.2 Microbiology

6.5.2.1 Clients are encouraged, but not required, to keep drinking water samples at <10°C during delivery to the laboratory.

6.5.2.2 Source water samples are kept at <10°C during transit to the laboratory.

SECTION 7.0 QUALITY CONTROL CHECKS AND ROUTINES TO ASSESS PRECISION, ACCURACY, AND METHOD DETECTION LIMITS (MDL)

The laboratory conducts testing in accordance with NIST traceability and all testing is NIST traceable. In instances where traceability to national standards of measurement is not applicable, the laboratory utilizes reference materials and proficiency testing to provide satisfactory evidence of correlation of results. The following describes typical quality control checks performed throughout the laboratory. It also describes specific QC checks and their acceptance criteria for each Inorganic and Organic section of the laboratory.

7.1 BLANKS

Blanks may be obtained from either the client or the laboratory. Trip, field, and equipment blanks are provided by the client to the laboratory for analysis. Blanks are routinely analyzed throughout the laboratory with each batch of samples. For Industrial Hygiene work only, blanks are used in sample correction and are analyzed with each batch of samples.

7.1.1 Method Blanks or Preparation Blanks

A method blank is an analytical control consisting of all reagents, internal standards, and surrogate standards that are carried through the entire analytical procedure. The method blank is used to define the level of laboratory background and reagent contamination. A method blank solution comes from the DI water system, treated as a sample for the parameters being measured, including all pre-treatment and preparation procedures. A method blank is prepared (extracted/digested/analyzed) for each batch of samples prepared in the laboratory.

7.1.1.1 The DI water system is checked daily to ensure the system is working properly. The light on the tank is checked and recorded. The conductivity of the water is also checked and recorded. If the conductivity is greater than 2.0 µmhos/cm than the Supervisor is notified immediately and the tanks are changed.

7.1.2 Instrument Blank/Calibration Blank & Reagent Blank

Used in the laboratory to detect contamination or interferences in the solvents and chemicals used to treat samples, which would systematically bias analytical results. They are used primarily when setting up an initial calibration curve or when analyzing continuing calibration verifications. Instrument blanks are performed on a daily basis to monitor contamination and carryover, accuracy, analyte drift, and some types of systematic bias.

A reagent blank is analyzed when trying to locate contamination in the reagent stock, which is used in sample preparation.

7.1.3 Client Blanks

A blank provided by the client is carried through the same analytical procedure as the samples.

- Trip Blank - This blank is prepared in the laboratory with deionized water, taken to the field and then brought back for analysis. The trip blank is not opened in the field. It serves as a check on sample contamination in the shipping and transport and from the site conditions. A trip blank is usually analyzed with each analytical batch or every 20 samples, whichever is greater. Trip blanks are analyzed for volatile compounds. A trip blank prepared with methanol may be used for volatile soil blank analysis utilizing EPA Method 5035.

- Field Blank - A field blank is exposed in the field to the same conditions that the samples are. It measures contamination during sampling in the field and shipping. It serves as a check on reagent and environmental contamination. A field blank, if available, should be analyzed with each analytical batch or every 20 samples, whichever is greater.

- Equipment Blank – An equipment blank is transported to the site, opened up and poured over or into the equipment that is used in collecting samples. This serves as a check on the sampling device cleanliness. One equipment blank, if available, should be analyzed for each analytical batch or every 20 samples, whichever is greater.

7.1.4 Blank Correction

Blank correction is not used when analyzing environmental samples. Blank correction is used only in industrial hygiene analysis.

- All blanks above the reporting limit should be discussed with the Department Supervisor.
- Client blank results are reported.
- Blank correction is only appropriate in the analysis of industrial hygiene samples.
- If suspected laboratory contamination in the blank, the results are reported and footnoted on the final report to the client, "suspected laboratory contamination".

7.2 SPIKES

7.2.1 Laboratory Control Samples (LCS)/Method Standards

An aliquot of laboratory reagent water is spiked with known quantities of the method analytes. The LCS is treated just like a sample and is used to determine whether the methodology is in control, whether the laboratory is in control and if the laboratory is capable of making accurate and precise measurements. An LCS is analyzed with each batch of samples prepared.

7.2.2 Matrix Spikes

7.2.2.1 Matrix spikes are environmental samples (soil or water) that are spiked with known concentrations of analytes that may be expected in the samples. The percent recoveries of the spiked analytes are taken as a measure of the bias of the analytical method caused by the sample matrix. They are calculated with the following equation:

$$\% \text{ Recovery (R)} = \frac{\text{(Concentration in Spike Sample – Conc. In Sample)}}{\text{Concentration Added}} \times 100$$

Matrix spikes and matrix spike duplicates are run with each analytical batch or every 20 samples, whichever is greater. The MS/MSD indicates the appropriateness of the method for the matrix by measuring recovery. If all of the samples in a given batch are suspected to contain high levels of analytes, a sample duplicate or blank spike may be substituted.

The appropriate use of matrix spikes is to evaluate method performance in the matrix, not laboratory performance. They are indicative of the overall bias and precision of a given batch of samples. Matrix spikes also monitor matrix interferences that may occur when running client samples.

7.2.2.2 Blank Spikes or Reagent Water Spikes are blank solutions that are fortified with known concentrations of analytes that may be expected in environmental samples. These spikes may or may not be taken through the full analytical procedure prior to analysis. The percent recoveries of the spiked analytes are taken as a measure of control of the analytical system.

7.3 INDEPENDENT QUALITY CONTROL CHECK SAMPLES (PTs)

Brighton Analytical participates in water pollution studies on a semi-annual basis (approximately every 6 months) and annual basis for drinking water testing. Environmental Resource Assoc. (ERA) provide the laboratory with the single blind samples and results are reported directly to ERA by the laboratory. ERA then reports the results directly to the State of Michigan (Drinking water Certification) and the Louisiana EPA (LELAP) prior to releasing the results to Brighton Analytical, LLC. This check sample is used to monitor the accuracy of the analyst and the system utilized for the particular test.

Check samples may come from sources such as independent certified reference materials (external suppliers), clients, or Brighton Analytical, LLC may prepare single or double blind samples. PT samples are always treated in the same manner as a regular sample. This includes managed, analyzed, and reported utilizing the same staff, methods, analysis, procedures, equipment, facilities, and frequency of analysis as if it were a real environmental sample. All PT samples are analyzed at Brighton Analytical, LLC and the laboratory does not communicate with other laboratories for information regarding PT samples. All data generated from PT samples including bench sheets, instrument printouts, data calculations, and data reports are maintained for a minimum of 5 years.

7.3.1 Performance (Proficiency) Testing (PTs) Requirements

State of MI requires one acceptable PT per calendar year. NELAP requirement: Laboratory must have acceptable results from the last 2 out of 3 most recent studies. For NELAP, if the laboratory fails 2 out of the most recent 3 studies, the laboratory's accreditation is suspended. If the laboratory fails 3 times in a row for a particular analyte, accreditation is revoked. The laboratory must analyze 2 successful PT studies in a row to be re-accredited. Any analytes that fail a study are researched to determine the cause of failure and corrective actions taken to correct the problem. All documented corrective actions are forwarded to Louisiana EPA which include the investigation and the action taken. All proficiency results are filed in the QA Office. Raw data is filed by each analyst.

7.4 STANDARDS AND CALIBRATIONS

7.4.1 Calibration Standards

7.4.1.1 Inorganic Analysis Calibration – The establishment of an analytical curve based on the absorbance, emission intensity, or other measured characteristics of known standards. The calibration standards are prepared using the same type of acid and reagents as used in the sample preparation (matrix matching).

7.4.1.2 Organic Analysis Calibration – A series of known standard solutions used by the analyst for calibration of the instrument, i.e., preparation of the analytical curve. A DI water solution containing the compound(s) of interest in a known concentration. Various dilutions of the standard are used to establish calibration curves. Calibration standards are analyzed on a daily or per method requirement basis. These standards monitor the accuracy and precision of the instrument.

7.4.2 Initial Calibration

The initial calibration is the analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the analytical detector or method. Methods are always calibrated with a zero standard and at least three concentration levels.

7.4.2.1 The lowest calibration standard cannot be less than the instrument detection limit but should be at or near the reported detection limit. The second point should correspond to the midpoint of the calibration range and the third point should be at the upper limit of the linear range. The specific method is referenced in regards to the number of calibration levels to be analyzed.

7.4.3 Calibration Verification

A calibration verification is a second source solution containing the compounds of interest in a known concentration different (e.g., different vendor or same vendor/different lot number) from the original standards used in the calibration curve. It is used to check the stability of the calibration curve and the calibration standards accuracy. This check monitors the accuracy and precision of the system and/or the analyst. Some methods, e.g., volatile organics, require a verification only after an initial calibration curve is run. Other methods require verification only when the standard is first prepared. The analyst follows method specific requirements when analyzing standards. Unless specific methods override, second source verification standards are made at the mid-level concentration of the analytical curve and the response within $\pm$10% of the initial calibration response. If method requirements are more stringent then method requirements apply.

7.4.4 Continuing Calibration Standards/Calibration Check Standards

7.4.4.1 Calibration curves must be verified at the beginning of each analytical run by analyzing at least a single-point, midrange continuing calibration check (CCC) standard. Samples analyzed on any given day must be bracketed by the initial calibration standards for quantitation (between the lower and upper limit of the calibration standards). If the samples are outside the range, they must be diluted and reanalyzed.

7.4.4.2 If instrument conditions change, e.g., new GC column, new AA tubes, gas flows, new detector, etc., a new initial calibration must be performed.

7.4.4.3 A CCC is also analyzed after the last sample is analyzed in a run (in analysis without surrogate standards). This will verify the instrument is still properly calibrated. If the CCC does not meet specific method criteria, samples analyzed since the last acceptable continuing calibration must be reanalyzed.

7.4.5 Quality Control Check Standard

(Laboratory Control Sample [LCS], Blank Spike, Laboratory Fortified Blank)

A solution containing the compound(s) of interest and taken through the entire analytical method. It may be made by someone other than the analyst or from an alternative source than the calibration standards. The analyst performing the analysis knows the concentrations. This spike is run at a frequency of 5% or every analytical batch. It monitors the accuracy and precision of the system and analyst.

7.4.6 Duplicates

7.4.6.1 Duplicate Samples are two aliquots of a sample that are taken through the laboratory's entire analytical method. Duplicate samples are usually only performed at the client's request or when the client submits a duplicate from the field.

7.4.6.2 Matrix Spike Duplicates

Matrix spikes are duplicates of an environmental sample that are spiked with the same compounds and at the same concentrations with the analytes of interest prior to extraction or digestion (if required by procedure). Recovery for each spiked analyte and RPD between the two recoveries is calculated. Matrix spikes/matrix spike duplicates are prepared at a minimum every 20 samples within Brighton Analytical, LLC. Follow method specific criteria for RPD.

7.4.6.3 Frequency and Acceptable Limits

Duplicate analyses for matrix spikes, samples, and laboratory control samples are performed at a rate dictated within each individual method. If frequency is not stated within the method, the laboratory requires a minimum of 10% of duplicates run within the laboratory.

The relative percent deviation (RPD) must be within 20%. If the %RPD is greater than 20%, the sample is reanalyzed if time allows. If the same results are generated, the data is noted by the analyst and the department supervisor is notified. To calculate %RPD:

$$\%RPD = \frac{[(\text{Replicate 1})-(\text{Replicate 2})]}{X\ (\text{mean})} \times 100$$

7.5 ADDITIONAL QUALITY CONTROL CHECKS

7.5.1 Internal Standards

A known amount of a compound, not expected to be found in the sample, is added to the sample just prior to instrumental analysis. These internal standard compound(s) are added to every standard, blank, matrix spike, matrix spike duplicate, sample (for VOAs), and sample extracts (for semi-volatiles) at a known concentration, prior to analysis. Internal standard(s) are used as the basis for quantitation of the target compounds. The response of this compound(s) audits the accuracy and precision of the results from the instrument for that sample matrix. They monitor accuracy and precision of the system and also matrix effects.

7.5.2 Surrogate Standards

Surrogates are organic compounds which are similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in environmental samples. These compounds are spiked into all blanks, calibration and check standards, samples (including duplicates and QC reference samples) and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate. Surrogates are used in all organic analysis. Surrogates monitor the overall efficiency of a method by imitating the analysis of the compounds of interest.

Surrogates are spiked at a concentration specified in the method. They must fall within the control limits established in accordance with the method. If criteria are not met, corrective action must take place. If no limits are established, use default of 80–120%.

Dilutions of the sample prior to analysis or matrix interference may take place during analysis and surrogate percent recovery cannot be achieved. In this case, emphasis should be placed on the other quality control within the sample batch.

7.5.3 Method of Standard Additions

In inorganic analyses, when severe matrix interference is demonstrated, the method of standard additions is employed.

7.6 FORMULAS TO CALCULATE PRECISION & ACCURACY

7.6.1 **Accuracy** is defined as the nearness of a result or the mean (x) of a set of results to the true value. Accuracy is assessed by means of reference samples and percent recoveries. Accuracy defines the relationship between the laboratory's measurement of a sample or standard's concentration and the "true" concentration in a sample are unknown, accuracy of sample results must be indirectly measured. Generally, this assessment is accomplished using percent recovery of matrix spike determinations to assess matrix effects. The percent recovery of standards is used to assess laboratory accuracy. Percent recovery is calculated as:

For Spiked Samples

$$\% \text{ Recovery} = \frac{SS - US}{S} \times 100$$

SS = Concentration of analyte in the spiked sample.
US = Concentration of the analyte in the unspiked sample.
S = Concentration of the analyte added to the sample.

For Standards

$$\% \text{ Recovery} = \frac{\text{Concentration Found}}{\text{True Concentration}} \times 100$$

7.6.2 **Precision** is the assessment of the variability that can be expected in data that result from the procedures employed. It is the agreement between a set of replicate measurements without assumption of knowledge of the true value. Precision is assessed by means of duplicate/replicate sample analysis. Precision is measured at Brighton Analytical using relative percent difference (RPD). RPD is calculated as follows:

$$RPD = \frac{(MS) - (MSD)}{(MS + MSD)(0.5)} \times 100$$

MS = Concentration of the analyte in the sample (or the spike recovery, with matrix spike duplicates)

MSD = Concentration of the analyte in the sample duplicate (or the spike recovery with matrix spike duplicates)

7.7 DILUTIONS

Samples are diluted when an analyte of concern is over the linear range of the calibration or when a matrix is too complex. Samples are diluted with a solution that is identical to the method blank or zero-standard, e.g., eluent, acid dilution, deionized water or solvent.

7.8 SAMPLE HOMOGENEITY

Samples are homogenized before preparation and/or analysis, including water and soil samples.

7.8.1 If the entire sample is used during preparation for the analysis, homogeneity is not an issue.

7.8.2 If a portion of the sample is used for preparation, the entire sample must be mixed thoroughly before taking a portion of it.

7.9 QUALITY CONTROL CHARTS

Quality control charts are assembled in all laboratory sections for laboratory control samples. Brighton Analytical also generates control limits for matrix spike/duplicate QC for client reference. The Quality Assurance Manager maintains control charts for regulatory purposes. The charts are based on both historical and method specific control limits. Internally generated QC ranges are never wider than method specific control limits. Historical warning limits are set at two times the standard deviation of the QC data and ranges are set at 3 times the standard deviation of the QC data. The charts are used to supplement method specific quality control limits and to forewarn of systematic method bias. The limits are updated every 6 months but monitored monthly for trends. Occasionally, updates may take place on a more frequent basis, e.g., a trend is developing and may warrant an update, etc. Corrective action is initiated if control charts indicate analytical or analyst performance problems.

7.10 DETECTION LIMITS

7.10.1 Instrument Detection Limit (IDL)

The IDL is the minimum amount of an analyte that can be reliably detected by the instrument. The IDL is the amount of analyte required to produce a signal that is 3 times the standard deviation of the background noise level. It is determined by multiplying by 3 the standard deviation obtained for the analysis of a standard solution (each analyte in reagent water) at a concentration of 3 to 5 times the IDL on three nonconsecutive days with seven consecutive measurements per day. See example below:

ANALYSIS 0.2 mg/L Std	RESPONSE
#1	0.025
#2	0.024
#3	0.024
#4	0.025
#5	0.023
#6	0.025
#7	0.024

Caluculate the mean ($\bar{x}$) and the standard deviation (s).

$\bar{x}$ = 0.02429
s = 0.00076

IDL = Day 1 $\quad \frac{\text{Conc. Of the Standard x 3s}}{\text{X}} = \frac{\text{0.2 mg/L x 3(0.00076)}}{\text{0.02429}} = 0.019$ mg/L

IDL = Day 2 0.021 mg/L

IDL = Day 3 0.0209 mg/L

Instrument Detection Limit (IDL) is = 0.02 mg/L

After determining the IDL, prepare a standard at this concentration and analyze to verify the instrument can detect it.

7.10.2 Method Detection Limit (MDL)

See Brighton Analytical SOP #BA003 for additional information on performing Method Detection Limits. Brighton Analytical uses the procedure listed in 40 CFR Part 136, Appendix C to determine method detection limits. MDLs may be performed as part of the method validation and analyst qualification procedures at the laboratory.

The Method Detection Limit is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. The Method Detection Limit is the constituent concentration that, when processed through the complete method, produces a signal with a 99% probability that it is different from the blank.

To determine the MDL, follow the procedure (1-9) below:

1. Make an estimate of the MDL using one of the following:
   a. The concentration value of 2.5 to 3 times the signal to noise ratio of the instrument.
   b. The concentration equivalent to 3 times the standard deviation of the replicate instrumental measurements of the analyte in reagent water.
   c. Area of the standard curve where there are significant changes in sensitivity such as a break in the slope of the standard curve.
   d. Within the instruments limitations.

2. Prepare reagent water that is free from interference or contamination of analytes of interest. Reagent water should be free of contaminants at the method detection level. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species. The interferent should be evenly distributed throughout the representative samples of a given matrix.

3. Prepare a standard that will produce a final concentration of 3 to 5 times the expected MDL when spiked into reagent water blanks.

4. Prepare a minimum of 7 aliquots of laboratory reagent water spikes for water MDLs or sodium sulfate/analyte free soil for soil MDLs. Also prepare at least 1 blank.

5. Analyze the replicates and blank(s) according to the method being followed.

6. Calculate the MDL as follows:

MDL = $t_{(n-1, 99\%)}$ x S

S = standard deviation of the replicate analyses.

t = Student's t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.

Number of Replicates	Degrees of Freedom (n-1)	Student's t t (n-1, .99)
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821

7. When reporting the MDL, the analytical method used must be specifically identified by number of title and the MDL must be expressed in the appropriate method reporting units. If the analytical method permits options that affect the MDL, these conditions must be specified with the MDL. Also the sample matrix and the concentration of the standard used must be identified on the report. For Drinking Water MDLs - the MDL report must include average % recovery of each analyte that was measured and the analytes must be within 80 – 120%, otherwise the MDL must be repeated for all analytes that fall outside this criteria. (State of Michigan Drinking Water Certification requirement, 1998).

8. MDLs for environmental methods are verified on an annual basis. Major changes in instrumentation would warrant an MDL study more frequent than once a year. These major changes in instrumentation may include, but not limited to, replacement or addition of equipment, changing of detectors, a new electron multiplier, etc.

9. An MDL is not required on a specific test if any component for which spiking solutions or quality control samples are not available such as temperature.

7.10.3 Limit of Detection (LOD)

Brighton Analytical determines the LOD for the method of each target analyte of concern in the quality system matrices. All sample-processing steps of the analytical method are included in the determination of the LOD. The LOD is confirmed by qualitative identification of the analyte(s) in a quality control sample in each quality system matrix containing the analyte at no more than 2-3x the LOD for single analyte tests and 1-4x the LOD for multiple analyte tests. This verification is performed on every instrument that is used to analyze samples and reporting of data. An LOD study is not performed for any component for which spiking solutions or quality control samples are not available such as temperature or when test results are not to be reported to the LOD.

7.10.4 Limit of Quantitation (LOQ)

The LOQ is confirmed by successful analysis of a quality control sample containing the analytes of concern in each quality system matrix 1-2 times the claimed LOQ. The recovery of each analyte is within the established test method acceptance criteria or client data quality objectives for accuracy. This single analysis is not required if the bias and precision of the measurement system is evaluated at the LOQ.

The reporting limits that Brighton Analytical provides to clients are reported at or above the LOD. As a general rule, the reporting limit is 10x the LOD. The reporting limit is established based on the MDL, regulatory limits, matrix of sample, and client needs. Interference or dilutions made to samples are noted on the final report and reflected in the reporting limit. Brighton Analytical does not report results outside the LOQ without qualification that the result is outside the range.

7.11 RETENTION TIME WINDOWS

Retention time windows are crucial to the identification of target compounds. They are used for compound identification in all GC and HPLC methods that do not employ internal standard calibration. Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample matrix and normal chromatographic variability.

7.11.1 Retention time windows are established in the following manner:

- Make three injections of a standard containing the target compounds over a 72- hour period. Injections made over a time period less than 72-hours will result in windows that are too narrow. Tight retention time windows may result in false negatives and/or may cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified.

- Record the retention time for each single component analyte and surrogate three decimal places. Calculate the mean and standard deviation of the three retention times for each compound. For multi-component analytes, choose three to five major peaks and calculate the mean and standard deviation of those peaks.

- Retention time windows are set at ±3 standard deviations of the mean absolute retention time.

- Establish the center of the retention time window for each analyte and surrogate by using the absolute retention time for each analyte and surrogate from the calibration verification standard at the beginning of the analytical shift.

A good indicator of retention time shifts are the surrogates. Whenever an observed retention time of a surrogate is outside of the established retention time window, the analyst determines the cause and corrects the problem before continuing analyses.

7.12 CALIBRATION VERIFICATION

The calibration established must be verified at periodic intervals. The process of verification applies to both external and internal calibration techniques and linear and non-linear calibration.
Refer to Brighton Analytical SOPs for method specific criteria.

7.13 CONFIRMATION

Several analyses performed at Brighton Analytical require the use of a second column confirmation. See the SOP for specific method requirements. Results obtained from the primary column are reported to the client. The secondary column is a separate instrument used only for identification to confirm the primary column.

SECTION 8.0 DATA REDUCTION, VALIDATION AND TRANSFER

8.1 ESTIMATION OF MEASUREMENT UNCERTAINTY

Uncertainty expresses the range of values that can be reasonably be attributed to the measured quantity. The expanded uncertainty provides the uncertainty at a level of confidence that the value actually lies within that range. The expanded uncertainty is usually expressed at the 95% confidence level.

8.1.1 Measurement uncertainty is defined as the sum of:

- the test method uncertainty
- the preparation method uncertainty
- the matrix interference uncertainty
- the sampling uncertainty

These elements encompass the uncertainties of the numerous steps of the analytical process including, but not limited to, sample plan variability, spatial and temporal sample variation, sample heterogeneity, calibration/calibration check variability, extraction variability, and weighing variability.

Brighton Analytical has procedures for estimating uncertainty of measurement using laboratory control sample (LCS - Method Standards) data that estimates the sum of the uncertainties of the first three elements above at the 95% confidence level. Brighton Analytical is not involved in sampling, so the LCS data is used to approximate uncertainty associated with the components within the laboratory's control.

An Uncertainty Table specifying the range for each analyte has been developed and is available when requested. If fewer that 20 data points are available, Best Professional Judgement (BPJ) is used until sufficient data are available.

8.1.2 The uncertainty for each analyte is calculated as follows:

- Use current LCS mean and standard deviation for each analyte of interest
- Calculate uncertainty as a ±value using mean +/- 2 standard deviations.

Example: Mean Recovery (X) = $\overline{93}$% Standard deviation = 5.2%

$$\text{Uncertainty} = \pm \frac{(2)(\text{stand. dev.})}{(X)} = \pm \frac{(2)(5.2)}{(93)} = \pm 11.2\%$$

For this analyte in this example, the uncetainty of the measurement is ±11.2%.

8.2 ANALYST RESPONSIBILTIES

Analysts have the following responsibilities in the area of collection and reduction:

- To follow applicable methods (EPA and other) and laboratory SOPs. Analysts must sign off on each applicable SOP stating that they have read, understand, and using the most current version of the method documentation. This is placed in the training file of each employee.
- To accurately transfer sample label numbers into instrument data files.
- To assure all method QC criteria are met or that appropriate data flags are added where criteria could not be achieved.
- To review all manual calculations (where applicable).
- To make single line strikeouts with name and date whenever corrections are necessary and to never employ the use of "White-out" products on any data generated.
- Promptly "work-up" data and give to data entry personnel within 2 days of sample analysis.
- When corrective actions issued, promptly investigate the QC data problem and document the deficiencies.

8.3 QUANTITATION

8.3.1 Sample Quantitation

Samples and quality control results are manually calculated where necessary. These calculations are taken directly from the applicable EPA methods and are documented in Brighton Analyticals SOPs.

8.3.2 Multiple Peak Quantitation

Calculation of analytes that require multiple peak matching are susceptible to matrix interference. Analyses such as PCBs, Gasoline, Diesel, and Toxaphene require matching of patterns for identification. Seventy to eighty percent of the major peaks must match for the analysis to be rendered positive. It is important to have trained personnel with experience to determine if patterns are positive or non-detect.

8.4 DATA TRANSFER AND ENTRY.

Brighton Analytical, LLC has implemented procedures to ensure that data transfers are free from errors, and that information is not lost during the transfers. When an analyst completes an analysis batch, the information is written up on a cover sheet for the data entry personnel to retrieve the numbers and also put results onto sheets that are produced by sample control when samples are initially logged into the computer system. The results on the sample control sheets and the results entered into the computer by data entry personnel are reviewed by the Laboratory Director for error. If the results match, the final report is signed off and sent to the client. If the results do not match, the raw data is reviewed and the Laboratory Director locates and corrects the error.

8.5 REPORTING DATA

Reports at Brighton Analytical are generated from data accumulated in the Laboratory Information Management System (LIMS). Final reports include, but are not limited to the following:

- Client Project Number and Name
- Date submitted to the laboratory

- Sampling date
- Analytical results
- Analysis date
- Detection limit and unit of measurement for each analysis type
- Analytical method
- Analyst's initials - person responsible for producing the results
- Date extracted/digested – if applicable
- Brighton Analytical, LLC Sample Identification
- Any statement(s) qualifying the data
- Signature and date indicating data was reviewed and approved by an authorized Brighton Analytical, LLC representative
- Cover letter (generated on Brighton Analytical, LLC letterhead)
  - Date report generated
  - Client information
  - Client project number and description
  - Brighton Analytical's project number

Unless otherwise requested by the customer, it is standard procedure to send representative batch quality control of precision and accuracy to the customer for every analysis performed. Data must be from the same batch that the customers' samples were analyzed. The client may request special batch quality control that is performed on the client's samples.

8.6 ENVIRONMENTAL CALCULATIONS

8.6.1 Percent Solids

All sediment/soil results at Brighton Analytical, LLC are calculated on a dry weight basis if a percent solid is determined. The sample result from the instrument is divided by the percent solid to give the reported result.

8.6.2 Reporting and the use of Significant Figures

All data at Brighton Analytical, LLC are reported with two significant figures. When data is reported out near the detection limit, only one significant figure is reported. The rules for calculating significant figures are listed below:

1. All digits that are not zero are significant.
2. In a number without a decimal point, zeros at the end are not significant.
3. In a number with a decimal point, zeros must be preceded by a non-zero digit to be significant. For example, [11,000, 1.0 , 0.0011] all contain two significant figures.

Listed below are examples of determining significant figures for final reports:
Example:
The reporting limit is 0.5 for an analysis. The value calculated may be 1 or 2 significant figures depending on the result of the analysis.

Analytical Result	Reported Result
0.4952	<0.5 *
0.5121	0.5 (1 sig fig)
1.7124	1.7 (2 sig fig)
10.4121	10 (2 sig fig)
106.2545	110 (2 sig fig)

- NOTE: Any result that is below the reporting limit, even if it rounds up to a positive hit, does not get rounded up.

8.6.3 Rounding

Brighton Analytical, LLC uses the following information in rounding data:

If the number following those to be retained is less than 5, the figure is dropped, and the retained figures are kept unchanged. As an example, 11.442 is rounded to 11.44.

If the number following those to be retained is greater than 5, the figure is dropped, and the last retained figure is raised by 1. As an example, 11.446 is rounded to 11.45.

If the number following those to be retained is 5, and if there are no figures other than zeros beyond the 5, the figure 5 is dropped, and the last-place figure retained is increased by one if it is an odd number or it is kept unchanged if an even number. As an example, 11.435 is rounded to 11.44, while 11.425 is rounded to 11.42.

Listed below are more examples of the rounding procedures performed at the laboratory:

Analytical Result	Rounded Result
0.8456	0.85
1.4500	1.4
9.7750	9.8
10.3621	10
110.9999	110
225.0000	220
225.1212	230

8.7 DATA VALIDATION

Data validation refers to the processes through which data are accepted or rejected. Brighton Analytical's SOPs provide criteria for the acceptability of resultant data. These documents also detail corrective actions employees must take when data fails to meet the specified limits of acceptability. All data must demonstrate and document the attainment of statistical control before it is reported. Calibrations, method blanks/standards (LCSs), matrix spikes/duplicates, and continuing calibration standards must meet all the method specific criteria listed in each SOP before data is submitted to Data Entry personnel. Unacceptable data should be returned to the analyst and a corrective action plan initiated by the data reviewer.

8.7.1 Data Validation Responsibilities/Data Review

The main aspect of data validation is laboratory data review. When an analyst produces results that are to be reported, they first evaluate each piece of associated data to determine whether all the requirements of the SOP have been met. Once this is determined, the analyst forwards data to their supervisor designated as a data reviewer who must also be competent in the SOP procedures. The Department Supervisor checks the raw data to confirm identification and reviews the calculations for accuracy. The Supervisor reviews the data package to determine if all the applicable requirements have been met. When all requirements are met, Supervisors sign off and releases the data to data entry personnel. If problems arise with the data, corrective actions are initiated and resolved before data is released. All corrective actions are formalized and written up in a report within 2 weeks after the initial corrective action write-up.

8.7.2 Laboratory Analysts Responsibilities

Laboratory analysts are responsible for the following duties related to data integrity:

- Checking all data calculations. The analyst's initials and date documents that this activity was done.
- Accurately entering and reviewing information into instrument logbooks relating to preventative maintenance, troubleshooting and instrument repair. The analyst's initials, date and record of activity document needed information in this area. All logbooks undergo supervisory review which is documented by the supervisor's signature (the supervisor signs once to document review of multiple pages).

- It is the analyst's responsibility to review results from calibration checks.

The above analyst activities are subject to routine self audits within each laboratory section. Additionally, the Quality Assurance Manager and Laboratory Director conduct routine targeted audits covering data integrity, laboratory logbooks, etc.

8.7.3 Data Validation Acceptance Criteria

Each analyst is familiar with the quality control criteria to be met for the analyses they are performing. Efforts are made to perform immediate corrective actions during analysis should problems arise. Analysts have the experience to abort analytical runs that will not pass basic QC criteria. The general guidelines for aborting analytical data are:

- Calibration data or continuing calibration data did not meet method defined criteria, or QC check standards or External Reference Sample did not meet criteria and will trigger reanalysis, then possibly termination of the analytical run if acceptable data are not obtained.
- Blank data is significantly above the method blank criteria along with other contamination indicators (i.e., high bias for check standards, matrix spikes or blank spikes) which would result in termination of the run.
- Holding time was exceeded. The client is contacted to determine if data are still usable and if so, data are flagged on the report.

8.7.3.1 Organics Department

Pesticides/PCBs/Herbicides: Surrogate recoveries that are lower or higher than the criteria results in a data flag or re-extraction/re-analysis of the sample.

GC/MS: Tuning criteria as defined in the method must be met. If it fails, rerun the tune. If the tune fails again, maintenance must take place. The tune must pass before any samples or standards are run. If the tune fails at the 12-hour check and will not pass, all samples must be rerun.

Surrogates must be within the limits established within the laboratory. If not, samples must be re-extracted and reanalyzed.

Internal standards must be within method criteria. If the criteria are not met, the sample is reanalyzed. If criteria are still not met, results are qualified.

Matrix spike recoveries must be within method criteria. If criteria is not met, and spike blank (laboratory control sample/method standard) passes, samples are flagged as having matrix effect.

8.7.3.2 Inorganics Department

Failed spikes and duplicates that are caused by matrix effects trigger one or more of the following set procedures:

- Metals- samples are diluted to reduce the effect of matrix interference.
- Diluted samples are rerun. If QC specifications still are not met and other quality control indicators indicate that the system is in control, the data is flagged.
- Matrix modifiers are only used in Graphite Furnace – AA to increase the volatilization temperature of the metal of interest and narrow the atomization range to improve response for all runs. Brighton Analytical does not analyze samples by the graphite furnace or Atomic Absorption methods.

8.8 ANALYTICAL RECORDS

It is the responsibility of each Brighton Analytical, LLC employee to keep complete records of all work and operations performed. All records generated at Brighton Analytical, LLC are company property. Data is archived to disk and can be retrieved for inspection and verification at any time. Records are kept in detail so that they can be understood by anyone reviewing the data. (For example, an analytical result for SW846 EPA Method 8260 can be traced back to the instrument that performed the test, raw data and calculations, tune and calibration that the number was calculated from, and also the standards used in calibrating the instrument) Unauthorized changes to, loss of, or destruction of records shall be grounds for disciplinary action and termination.

8.8.1 Retention of Analytical Data

Analytical data may include, but is not limited to, calibration curves, check standards, retention time windows, % drift, relative standard deviation, % difference, sample analyses, all quality control data produced to support sample analysis, etc.

1. Raw data will be legibly recorded on bench sheets or in bound laboratory notebooks using permanent ink.
2. Data in the form of charts, instrument recordings, and printouts will be clearly identified.
3. Analytical (raw) data will be filed by analysis and date and held a minimum of ten years. Microbiological data is kept a minimum of five years.
4. Each analytical data set includes, at a minimum, all quality control required and generated to produce the set, instrument raw data printouts, and curve (if generated prior to running samples).

8.8.2 Other Records

The Safe Drinking Water Act requires retention of records a minimum of 6 years and NELAC requires a minimum of 5 years of retention of records. All records at Brighton Analytical, including raw data, original observations, calculations and derived data, calibration records and copies of test reports, are retained and maintained a minimum of 6 years unless otherwise requested by the client.

Brighton Analytical's computer system is backed up on cassettes on a daily, weekly, monthly, quarterly, and yearly rotation. Data is also backed up on zip drives on an "as needed" basis when the LIMS system reaches capacity. The Laboratory Director stores the records in a separate storage area located at Brighton Analytical, LLC and is also responsible for monitoring the records.

SECTION 9.0 CORRECTIVE ACTIONS AND QUALITY CONTROL MEASURES

9.1 CORRECTIVE ACTIONS

Quality control measures are used at Brighton Analytical, LLC to monitor and assess the effectiveness and validity of sampling and analysis activities. If a specific quality control measure is determined to have failed to meet a prescribed level of performance, and the source or reason for the deviation is not identified and corrected, the sample data associated with the quality control measure may not be useful or valid. Corrective actions refer to the steps taken to resolve situations where the quality control measure is determined to be out of the predetermined acceptance range. Corrective actions must take place to restore proper in-control functioning of the system.

All corrective actions must be documented in order to ensure the problem encountered was followed up and completed within a reasonable amount of time. Any corrections or additions to any documentation in the laboratory must be initialed and dated. If information is crossed out, it must be done so with a single line through it. "White-Out" is not to be used at any level of the laboratory's documentation procedure including raw data, data reduction and write-up, final reports, quality control, etc.

Corrective action forms are available and employees are advised to use them whenever an error, out-of-control, or deficiency is noted. (See Figure 7.0- Brighton Analytical's Corrective Action Form)

9.1.1 Identifying and Assessing QC Measures

At Brighton Analytical, LLC, the analyst and supervisor of the department review quality control information. The responsibility for the initial assessment of a quality control measure lies with the individual who identifies the sample or procedure as a QC measure and has access to the test results.

9.1.1.1 Analyst Responsibilities

The person responsible for operating the analytical instrument or equipment must be responsible for assessing the following QC measures, where applicable:

1. Method, reagent and calibration blanks.
2. Calibration integrity: initial and continuing calibration, QC check standards and interference standards.
3. System Performance Checks
4. Tuning Criteria
5. Surrogate and internal standards
6. Titrating Solutions

9.1.1.2 Data Reviewer Responsibilities

The following checks are normally assessed where applicable by the analyst and a secondary reviewer:

1. Secondary reference material.
2. QC Check Samples/External Reference Samples
3. Spiked Samples (matrix and blank).
4. Duplicates.

9.1.1.3 Field Personnel/Sampler Responsibilities

Results from the following samples are assessed by clients of Brighton Analytical, LLC or individuals responsible for sample collection, but may be reviewed by laboratory personnel if the sample has been identified as:

1. Pre-cleaned and field cleaned equipment blanks.
2. Trip Blanks (number to be analyzed specified by client).
3. Field collected duplicates.
4. Split samples.

9.1.2 Determining the Source of the QC Problem

Once a problem has been identified, the reason for the problem must be discovered and/or corrected. If the sample analysis system is deemed to be out of control, the process should be halted until the problem has been addressed. Finding the source of a QC problem involves identifying probable sources of error, and checking each source to determine if protocols were properly followed. Common sources of error and suggested follow-up protocols are listed in Table 9.0 – Possible Sources of QC Problems and Suggested Corrective Actions. This listing does not preclude additional identification of other possible sources and associated follow-up protocol. The individual responsible for identifying the problem is responsible for determining the cause. Other Brighton Analytical, LLC employees can assist as needed.

9.1.3 Initiating and Documenting Corrective Action

Once the source of a QC error has been identified, appropriate steps are taken to eliminate or minimize re-occurrences. All laboratory personnel have the authority to stop work if a problem is suspected or encountered. Only a Laboratory Supervisor, the Laboratory Director or Quality Assurance Manager have the authority to start/resume work.

9.1.3.1 Corrective Action Initiating from the Analyst

If any QC measure causes the analytical system to be out of control, testing should not continue until the QC check meets specifications. Corrective actions may be initiated by:

1. The analyst operating the instrument.
2. The analyst's Supervisor, the Laboratory Director, or the QA Manager if the solution is not immediately apparent.

9.1.3.2 Corrective Action Initiation from the Data Reviewer

Corrective actions for QC measures that are identified by the reviewer must be initiated by that individual.

9.1.3.3 Documenting Corrective Actions

Documentation does not always imply a formal memo or corrective action form:

1. Corrective actions that are initiated during an on-going analytical run may be documented on the chromatogram or other pertinent analytical sheets as well as the instrument, analytical and/or field logs.
2. Corrective actions that require input or intervention of more than one individual must, at a minimum, be documented in the related logs and records. Corrective action forms may be used.
3. If more than one part of the organization or external help is involved with identifying a QC problem formal corrective action forms are recommended, although dated and signed phone logs are acceptable. In all cases, a copy of all documentation is maintained in the batch files.

If a quality control problem is identified during the analysis that affects more than one set of data or multiple projects, the documentation associated with identifying and resolving the problem is cross referenced to all associated projects. Clients of Brighton Analytical, LLC are promptly notified of QC failures that may affect their data. Affected samples are reanalyzed, re-sampled (if necessary) or are appropriately flagged in the case of QC failure with data qualifiers in the comment section of the final report.

Corrective actions may involve re-preparation including extracting, digesting, or volatile sample preparation. If the sample is re-prepared/analyzed and the results are identical to the first analysis (control for each analysis is method specific and can be located in the method specific SOPs), the data may be qualified and footnoted on the final report.

9.1.4 Corrective Actions Initiated From External Sources

The need to initiate corrective actions may be the result of activities or audits from external sources. Sources include systems audits, performance audits, split samples, blind QC samples, client complaints, and findings from project or data validation reviews. These must be initiated with a corrective action form and the QA Manager must be immediately notified. Once complete, all corrective action documentation is filed in the QA Manager's office for reference.

9.1.4.1 Client Complaints - Corrective actions that arise from client complaints begin with a client complaint corrective action form. (See Figure 8.0). The project number, sample identification and any pertinent information is recorded in addition to the problem. If data needs to be reviewed, the Laboratory Director or QA Manager will review the raw data to confirm the result(s) in question. If an error is discovered, the reviewer will verify the error with the analyst and re-submit the results to data entry for a revised report. If no errors are found and the client wants the sample to be re-analyzed, the project modification is given to data entry where the sample(s) is given a new due date and paperwork is generated for the analyst. All paperwork is kept with the report and a copy of the corrective action is filed in the Quality Assurance Office. For more information on corrective actions, see BA SOP #BA010.

9.1.4.2 Client complaints are handled immediately by customer service and usually resolved within one week or less.

9.2 PERFORMANCE AND SYSTEM AUDITS

9.2.1 Performance Audits

Performance audits are conducted at a specified frequency to determine the accuracy of a measurement system or its component parts. Performance audits at Brighton Analytical, LLC consist of the following:

9.2.1.1 Internal Performance Audits

1. Initial demonstration of analyst capability is performed after training has been completed on any analytical procedure. The analyst must demonstrate the ability to appropriately conduct the analytical protocol by analyzing a blind and/or quality control sample and obtaining results within a specified range for precision and accuracy. This demonstration must occur for each new analyst and for each new analysis that is performed.

2. Additional performance proficiency is demonstrated on a representative group of analyses set up as "blind" samples at a minimum of semi-annually or more frequently at the Laboratory Director's discretion.

9.2.1.2 External Performance Audits (PT Program)

Brighton Analytical, LLC participates in the Water Pollution (WP), Water Supply (WS) and Soil (HW) performance evaluation programs. These samples are used in Brighton Analytical's QA Program and for outside accrediting agencies. The results of the analyses are compiled and reported to the agency which had submitted the samples. When results are received, they are transmitted to each department and all results that are "not acceptable" must be investigated and a corrective action plan initiated. Many times a secondary set of blind reference samples are processed by the laboratory and the results reported directly to the regulatory agency.

9.2.2 System Audits

System audits consist of the review and evaluation of various components of a measurement system to determine the proper selection and use. System audits consist of the following:

- Detailed review of each component of the system.
- A determination that each element within an activity is functioning properly and within the guidelines of appropriate methodology, approved procedures, and the Quality Assurance Plan.
- A list of deficiencies that must be addressed to correct/improve or modify the system.

9.2.2.1 Internal System Audits

The following routine system audits (conducted by the Quality Department) occur at Brighton Analytical:

Routine system audits:

- Analytical batch reviews for each laboratory section. Batches are checked for conformance to applicable methods and SOP requirements. These reviews supplement the routine, supervisory review of all batch data performed before final data are reported.

- An audit may be initiated by the Laboratory Director to focus on any suspected problem areas at any time during the year. (See Figure 8.0-Internal Audit Checklist)

- Annual Audit Program: The Quality Department conducts a system internal audit annually per each analysis at Brighton Anaytical. A list of deficiencies or problems, if any, are detailed in corrective action plans. Monthly checks are then conducted to follow up the deficiencies from the internal audit to confirm compliance. All corrective actions and findings are followed up. Affected data is evaluated for impact. Clients are then informed of affected data and reports are footnoted and re-issued. If sample is within hold time, it is re-analyzed and re-reported to the client.

  Schedule for the annual audits are as follows:

  January, February, March - Wetchem department to include Ion Chromatography, Cyanides, Ammonia, Phenolics, TKN.
  April, May, June- The rest of wetchem including COD, BOD, Phosphorus, Flashpoint, pH, FOG.
  July, August, September - Organics department to include volatiles, TOC, semivolatiles, PCB, Pesticides, and Herbicides.
  October, November, December - Inorganics department to include metals by ICP/MS & Mercury. (Include login, data review, and report generation).

9.2.2.2 Annual Management Reviews

Annually the Laboratory Director and Quality Assurance Manager review the quality system and environmental testing activities to ensure their continuing suitability and effectiveness and to introduce necessary changes or improvements. This review by management takes into account:

- the suitability of policies and procedures;
- reports from managerial and supervisory personnel;
- the outcome of recent internal audits;
- corrective and preventative actions;
- assessments by external bodies;
- results of proficiency tests (PTs);
- changes in the volume and type of work;
- client feedback;
- complaints;
- other relevant factors, such as quality control activities, resources and staff training.

Findings from management reviews and the actions that arise from them are recorded and filed in the Quality Assurance Office. Management ensures that actions are carried out within an appropriate and agreed time-scale.

9.3 PREVENTATIVE ACTION

9.3.1 Preventative action is a pro-active process to identify opportunities for improvement rather than a reaction to the identification of problems or complaints.

9.3.2 Needed inprovements and potential sources of nonconformances, either technical or concerning the quality system are idenfified. If preventative action is required, action plans are developed, implemented and monitored to reduce the likelihood of the occurrence of such nonconformances and take advantage of the opportunities for improvement.

9.3.3 Topics that are annually reviewed by the Laboratory Director and Quality Assurance Manager include, but not limited to:

- Annual Management Review
- Annual Review of Standard Operating Procedures by the analyst's
- Preventative Maintenance procedures and routine maintenance procedures including instruments.
- Annual internal audits.

9.4 Maximum Contaminant Levels (MCL) in Drinking Water Samples

9.4.1 Notification Procedure

If an analyst determines that a drinking water sample exceeds an MCL, they immediately notify the Laboratory Director of the situation. The data is then reviewed in its entirety for completeness and acceptability. If the data confirms the measured concentration, the Laboratory Director or the General Manager contacts the client immediately. (See Table 10.0 – Maximum Contaminant Levels for Organic and Inorganic Compounds).

9.4.2 Confirmation of Analysis

9.4.2.1 The analyst re-tests the sample to confirm the hit. The client is informed of the initial result and that the sample is being re-analyzed to confirm the result.

9.4.2.2 Upon confirmation of the analysis, the client is informed either by phone or facsimile of the final result of the drinking water sample. If the client is a homeowner, the laboratory suggests to the homeowner to contact their water supplier and/or local health department.

9.4.2.3 A hardcopy of the results are sent out to the client which notes the test results and also the final report documents the MCL (if applicable).

TABLES

TABLE 1.0 BALANCE INVENTORY

BALANCE MODEL NO.	MANUFACTURER	SERIAL NO.	LOCATION IN LAB	MAX WEIGHING CAPACITY
SC4010	O'Haus Scout	BJ117456	Outside Login	400gms±0.01gms
TS4KD	O'Haus Scout	2796	Volatile Inst. Lab	4000gms±0.01gms
XS204	Mettler Toledo	1129381109	Dish Lab	220gms+0.1gms
A-200DS	Denver Inst. Co.	0062750	Wet-Chem	250gms ± 0.01gms
N18110	O'Haus Scout	D244009653	Extraction Lab	810gms ± 0.1gms
XL-3100	Denver Inst. Co.	N0107793	Extraction Lab	3100gms+0.01gms
PB3002-S	Mettler Toledo	1129392340	Dish Lab	3100gms±0.01gms
BA110S	Sartorius	30505064	Metals Lab	100gms ± 0.01gms
AG245	Mettler-Toledo	1116511222	Wet-Chem	250gms ± 0.01gms
CS-200	O'Haus Scout	CS200	SVOC Lab	200gms±0.1gms

TABLE 2.0 ANALYTICAL THERMOMETER INVENTORY

THERMOMETER	LOCATION IN Laboratory	USE:
NIST-traceable (#276999)	**Quality Assurance Office**	**Calibrating In-House Thermometers**
NIST-traceable (#9681)	**Quality Assurance Office**	**Calibrating In-House Thermometers**
BOMB	**Metals Prep/Glassware**	**Used in bomb analysis of samples**
BATH-1	**Extraction Lab**	**Monitoring temp. extraction water bath**
FLASH	**Metals Prep/Glassware**	**Monitor temperature flashpoint analysis**

Incubator #1 Micro Analysis	**Microbiology Lab**	**Incubator for Micro-Analysis**
Incubator #2 Micro Analysis	**Microbiology Lab**	**Incubator for Micro-Analysis**
Incubator #3 Micro Analysis	**Microbiology Lab**	**Incubator for Micro-Analysis**
MERCURY BATH	**Metals Laboratory**	**Monitoring the Hg bath temp.**
TSS/TDS	**Metals Laboratory**	**Monitoring the oven temperature.**

TABLE 3.0 REFRIGERATOR/FREEZER INVENTORY

UNIT NO.	LOCATION	REFRIGERATOR CONTENTS	FREEZER CONTENTS
BA-01	**VOL INST LAB**	**VOL SAMPLES-VOA VIALS & MEOH EXTRACTS**	**----------**
BA-02	**VOL INST LAB**	**----------**	**VOL STOCK & INTERMEDIATE STDS**
BA-03	**VOL INST LAB**	**SAMPLES HIGH IN SOLVENTS & VOLATILE SAMPLE STORAGE**	**ICE PACKS**
BA-05	**VOL INST LAB**	**PCB/PEST/HERB WORKING STDS METHANOL**	**----------**
BA-06	**WET-CHEM**	**STANDARDS, REAGENTS FOR WET-CHEM ANALYSIS**	**ICE PACKS**
BA-08	**WALK-IN #1 (HALLWAY NEAR EXTRACTIONS)**	**PRE-&POST ANALYSES SAMPLES, PRE-LOG-IN SAMPLES**	**----------**
BA-09	**WALK-IN #2 (STORAGE AREA BEHIND BA-08)**	**PRE- & POST ANALYSES SAMPLES**	**----------**
BA-10	**EXTRACTIONS**	**----------**	**EXTRACTED SAMPLES PRE-CONCENTRATED**
BA-11	**EXTRACTIONS**	**----------**	**STANDARDS USED IN EXTRACTIONS**
BA-12	**SEMI-VOL INST LAB**	**MICROBIOLOGY STANDARDS**	**SEMI-VOL STOCK & INTERMED. STANDARDS**
BA-13	**WALK-IN #3 (BACK STORAGE ROOM)**	**PRE- & POST ANALYSES SAMPLES**	**----------**

TABLE 4.0 Hazardous Waste Disposal Criteria

ANALYTE	LEACHATE SPLP/TCLP (µg/L)	SOIL/SOLID (µg/kg)	WATER, TOTAL (µg/L)
Volatile Hazardous Waste Disposal Criteria			
Benzene	500	10,000	500
Carbon tetrachloride	500	10,000	500
Chloroform	6,000	120,000	6,000
1,4-Dichlorobenzene	7,500	150,000	7,500
1,2-Dichloroethane	500	10,000	500
1,1-Dichloroethene	700	14,000	700
Methyl Ethyl Ketone (MEK)	200,000	4,000,000	200,000
Tetrachloroethene	700	14,000	700
Trichloroethene	500	10,000	500
Vinyl chloride	200	4,000	200
Semi-Volatile Hazardous Waste Disposal Criteria			

Chlorobenzene	100,000	2,000,000	100,000
o-Cresol	200,000	4,000,000	200,000
m-Cresol	200,000	4,000,000	200,000
p-Cresol	200,000	4,000,000	200,000
Total Cresols	200,000	4,000,000	200,000
2,4-Dinitrotoluene	130	2,600	130
Hexachlorobenzene	130	2,600	130
Hexachlorobutadiene	500	10,000	500
Hexachloroethane	3,000	60,000	3,000
Nitrobenzene	2,000	40,000	2,000
Pentachlorophenol	100,000	2,000,000	100,000
Pyridine	5,000	100,000	5,000
2,4,5-Trichlorophenol	400,000	8,000,000	400,000
2,4,6-Trichlorophenol	2,000	40,000	2,000
Pesticide Hazardous Waste Disposal Criteria			
Chlordane	30	600	30
Endrin	20	400	20
Heptachlor	8	160	8
Heptachlor epoxide	8	160	8
Lindane	400	8,000	400
Methoxychlor	10,000	200,000	10,000
Toxaphene	500	10,000	500
Metal Hazardous Waste Disposal Criteria			
Arsenic	5.0	100	5.0
Barium	100.0	2000	100.0
Cadmium	1.0	20	1.0
Chromium	5.0	100	5.0
Lead	5.0	100	5.0
Mercury	0.2	4.0	0.2
Selenium	1.0	20	1.0
Silver	5.0	100	5.0

TABLE 5.0 INSTRUMENT INVENTORY

QTY	DESCRIPTION
1	KONELAB Auto Colorimetric Analyzer
1	HP 4500 ICP/MS w/ autosampler
1	Agilent 7500ce series ICP/MS. Model #G3272A.
1	HP 5973 GC/MS: w/ EST/Varian Archon autosamplers and EST/Varian Encon concentrator.
1	Agilent 6890 GC/MS with autosampler/7890 GC/MS with autosampler..
1	HP5972 with Shimadzu AOC-20I autosampler.
2	Hewlett Packard 5890 GC with ECD/FID (HP-4) detectors with Cobra Liq. Sampler, FID detector (HP-3) with Tekmar 2000+2016 Purge and trap & 6890 series ECD.
1	Dionex ICS-2100 Ion Chromatography System with a DS6 Conductivity detector.
1	Perkin-Elmer Autosystem GC with dual PID detectors and Tekmar 2000+2016 purge & trap and Dynatech PTA-30 Tekmar 2000 purge and trap.
1	Hewlett-Packard 7890 duel injector, duel ECD GC with 7693 autosampler.
1	Leeman Labs Hydra AA Automated Mercury Analysis System PS200II
1	Leeman Direct Reading Echelle ICP with autosampler.
1	Leeman Teledyne Hydra II AEG Low Level Mercury Analyzer
1	Lachat Quickchem AE Automated Ion Analyzer with Block Digester and autosampler.
1	Dohrman DX-20A TOX/TX/EOX Analyzer
1	OI-Analytical FS3000 & RA Sample for Available Cyanide determination.
1	Perkin-Elmer Nelson Data Acquisition System (Turbochrom version 6.3.2.0:0646), LabWorks, Laboratory Info. Mngmt. System (LIMS).

QTY	DESCRIPTION
1	Accelerated Solvent Extractor (Dionex ASE 200)
1	Infrared Spectrophotometer
1	UV/VIS Spectrophotometer
1	Turbidity meter
1	Perkin-Elmer 200 HPLC w/ UV/VIS & autosampler & fluorescense detector
1	Perkin Elmer HPLC w series 200 A/S, pump, UV/VIS Detector & Fluorescence detector & BAS LC-4C EC detector
1	Shimadzu TOC-L Analyzer w/ ASI-L autosampler
5	TCLP Sample Tumblers
5	Zero Headspace extractors w/ tumblers
1	CEM Microwave Digestor
3	pH Meter/ NH3 probe, BOD probe, Fluoride probe.
9	Analytical Balances
2	Sample ultrasonicator
3	Fluorescence Spectrometer
1	Conductivity meter
1	Parr Oxygen Bomb, calorimeter
2	Flash Point analyzers (1 Manual & 1 Petrochem Petrotest Automated)
1	COD low range analyzer
1	Autoclave for coliform disposal (Harvey Hydroclave SC8)
3	Incubators for bacteria analyses (Thermolyne Type I42300,VWR 1510E & Low Temp 2020)

TABLE 6.0 HOLDING TIMES FOR ORGANIC & INORGANIC STANDARD SOLUTIONS

	EXPIRATION TIME
NEAT REAGENTS (expiration not specified by vendor)	10 Years
ORGANIC ANALYTES	
Volatile Standards	
Working Standards	1 Week
Secondary (Intermediate) Standards – Non-Gas	6 Months
Secondary (Intermediate) Standards – Gas	Weekly
Stock Standards – Non-Gas	Monthly
Stock Standards – Gas	Weekly
Matrix Spike Mix	6 Months
Bromofluorobenzene Solution	6 Months
Semi-Volatile Standards	
Calibration Check Standards	1 Week
Working Standards	1 Year
Stock Standards	6 Months
Matrix Spike Mix	6 Months
DFTPP Solution	6 Months
Pesticides/PCBs	
Working Standards	1 Week
Intermediate Standards	6 Months
Stock Standards	6 Months
Herbicides	
Free Acid Forms	2 Months
Derivatized Standards	1 Year
Metals	
Working Standards (less than 10ppm)	2 Weeks

Working Standards (10 to less than 500ppm)	6 Months
Working Standards (greater than 500ppm)	2 Years
Classical Chemistry (Wet Chem)	
Hexavalent Chromium – Intermediate Standards	2 Weeks
Hexavalent Chromium - Working Standards	1 Day
Nitrate/Nitrite & Orthophosphate Standards	1 Month
Other Stock Standards	6 Months
Other Working Standards	Monthly

TABLE 7.0 CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES FOR AQUEOUS MATRICES

Name	Container[1]	Preservation	Maximum Holding Time
INORGANIC TESTS:			
Chloride	Polyethylene, Glass	Non-required (NR)	28 days
Cyanide, total and amenable to chlorination	Polyethylene, Glass	Cool to 4°C; if oxidizing agents present add 5 mL 0.1N NaAsO2 per L or 0.06g of ascorbic acid per L; adjust pH>12 w/ 50% NaOH.	14 days
Hydrogen ion (pH)	Polyethylene, Glass	NR	15 minutes
Nitrate	Polyethylene, Glass	Cool to 4°C	48 hours
Sulfate	Polyethylene, Glass	Cool to 4°C	28 days
Sulfide	Polyethylene, Glass	Cool to 4°C, add zinc Acetate	7 days
Metals:			
Chromium VI	Polyethylene, Glass	Cool to 4°C	24 hours
Mercury	Polyethylene, Glass	HNO_3 to pH<2	28 days
All other metals	Polyethylene, Glass	HNO_3 to pH<2	6 months
ORGANIC TESTS:			
Acrolein & Acrylonitrile	Glass, PTFE-lined septum	Cool to 4°C, 0.008% $Na_2S_2O_3$[3], Adjust pH to 4-5	14 days
Benzidines	Glass, PTFE-lined cap	Cool to 4°C, 0.008% $Na_2S_2O_3$[3]	7 days until ext 40 days after extraction
Chlorinated Hydrocarbons	Glass, PTFE-lined cap	Cool to 4°C, 0.008% $Na_2S_2O_3$[3]	7 days until ext 40 days after extraction
Haloethers	Glass, PTFE-lined cap	Cool to 4°C, 0.008% $Na_2S_2O_3$[3]	7 days until ext 40 days after extraction
Nitroaromatics and cyclic ketones	Glass, PTFE-lined cap	Cool to 4°C, 0.008% $Na_2S_2O_3$[3]	7 days until ext 40 days after

			extraction
Nitrosamines	Glass, PTFE-lined cap	Cool to 4°C, 0.008% $Na_2S_2O_3$[3]	7 days until ext 40 days after Extraction
Oil & Grease	Glass	Cool to 4°C, add 5mL H_2SO_4	28 days
Total Organic Carbon (TOC)	Polyethylene or Glass	Cool to 4°C, store in dark[2]	28 days
Organochlorine Pesticides	Glass, PTFE-lined cap	Cool to 4°C	7 days until ext 40 days after extraction
Organophosphorus Pesticides	Glass, PTFE-lined cap	Cool to 4°C[4]	7 days until ext 40 days after extraction
PCBs	Glass, PTFE-lined cap	Cool to 4°C	7 days until ext 40 days after extraction
Phenols	Glass, PTFE-lined cap	Cool to 4°C, 0.008% $Na_2S_2O_3$[3]	7 days until ext 40 days after extraction
Phthalate esters	Glass, PTFE-lined cap	Cool to 4°C	7 days until ext/40 days after extraction
Polynuclear aromatic hydrocarbons	Glass, PTFE-lined cap	Cool to 4°C, 0. 008% $Na_2S_2O_3$[3] store in dark	7 days until ext/40 days after extraction
Purgeable aromatic Hydrocarbons	Glass, PTFE-lined septum	Cool to 4°C, 0.008% $Na_2S_2O_3$[2,3]	14 days
Purgeable halocarbons	Glass, PTFE-lined septum	Cool to 4°C, 0.008% $Na_2S_2O_3$[3]	14 days
Total Organic Halides (TOX)	Glass, PTFE-lined cap	Cool to 4°C, adjust to pH<2 w/ H_2SO_4	28 days
Microbiological Tests			
Drinking Water:			
Total coliforms, fecal coliforms or *E. coli*	Polyethylene or Glass, Pre-sterilized	Samples should be cooled to <10°C	30 hours for drinking water
Source Water:			
Total coliforms or fecal coliforms	Polyethylene or Glass, Pre-sterilized	Cool to <10°C.	8 hours

[1]Polyethylene (P) or Glass (G)
[2]Adjust pH<2 with H_2SO_4, HCl or solid $NaHSO_4$. Free chlorine must be removed prior to adjustment.
[3]Free chlorine must be removed by the appropriate addition of $Na_2S_2O_3$.
[4]Adjust samples to pH 5-8 using NaOH or H_2SO4.
** Partially excerpted from SW-846, Revision 3, December 1996.*

TABLE 8.0 CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES FOR SOLID MATRICES

Name	Container	Preservation	Maximum Holding Time
INORGANIC TESTS:			
Bromide	Polyethylene, Glass	Non-required (NR)	28 days
Hydrogen ion (pH)	Polyethylene, Glass	NR	15 minutes
Nitrate	Polyethylene, Glass	NR	28 days
Sulfate	Polyethylene, Glass	NR	28 days
Sulfide	Polyethylene, Glass	NR	7 days
Metals:			
Chromium VI	Polyethylene, Glass	NR	28 days
Mercury	Polyethylene, Glass	NR	28 days
All other metals	Polyethylene, Glass	NR	6 months
ORGANIC TESTS:			
Acrolein & Acrylonitrile	Glass, PTFE-lined septum	Cool to 4°C	14 days
Benzidines	Glass, PTFE-lined cap	Cool to 4°C	14 days until ext 40 days after extraction
Chlorinated Hydrocarbons	Glass, PTFE-lined cap	Cool to 4°C	14 days until ext 40 days after extraction
Haloethers	Glass, PTFE-lined cap	Cool to 4°C	14 days until ext 40 days after extraction
Nitroaromatics and cyclic ketones	Glass, PTFE-lined cap	Cool to 4°C	14 days until ext 40 days after extraction
Nitrosamines	Glass, PTFE-lined cap	Cool to 4°C	14 days until ext 40 days after extraction
Total Organic Carbon (TOC)	Polyethylene or Glass	Cool to 4°C, store in dark	28 days
Organochlorine Pesticides	Glass, PTFE-lined cap	Cool to 4°C	14 days until ext 40 days after extraction
Organophosphorus Pesticides	Glass, PTFE-lined cap	Cool to 4°C	14 days until ext 40 days after ext.
PCBs	Glass, PTFE-lined cap	Cool to 4°C	14 days until ext

			40 days after ext
Phenols	**Glass, PTFE-lined cap**	**Cool to 4°C,**	**14 days until ext 40 days after ext**
Phthalate esters	**Glass, PTFE-lined cap**	**Cool to 4°C**	**14 days until ext 40 days after ext**
Polynuclear aromatic hydrocarbons	**Glass, PTFE-lined cap**	**Cool to 4°C, store in dark**	**14 days until ext 40 days after ext**
Purgeable aromatic Hydrocarbons	**Glass, PTFE-lined septum**	**Cool to 4°C,**	**14 days**
Purgeable halocarbons	**Glass, PTFE-lined septum**	**Cool to 4°C,**	**14 days**
Total Organic Halides (TOX)/TX/EOX	**Glass, PTFE-lined cap**	**Cool to 4°C**	**28 days**

Microbiological Tests

Total coliforms, fecal coliforms or E. coli	**Polyethylene or Glass, Pre-sterilized**	**Samples should be cooled to <10°C**	**30 hours or less**

[1]Polyethylene (P) or Glass (G)
[2]Adjust pH<2 with H_2SO_4, HCl or solid $NaHSO_4$. Free chlorine must be removed prior to adjustment.
[3]Free chlorine must be removed by the appropriate addition of $Na_2S_2O_3$.
[4]Adjust samples to pH 5-8 using NaOH or H_2SO_4.

TABLE 9.0

POSSIBLE SOURCES OF QC PROBLEMS AND SUGGESTED CORRECTIVE ACTIONS

1) CALIBRATIONS

a. Sources and expected review procedures:
   1. Improperly prepared or outdated standards – review preparation logs for calculation/dilution errors and use of expired sources.
   2. Improperly prepared or outdated check standard – verify check standard.
   3. Poor instrument response – determine if preventative maintenance is required.
   4. Incorrect calculations – review and verify all calculations.
   5. Contamination problems (see blanks #2).

b. Expected corrective actions:
   1. Recalculate calibration curve.
   2. Prepare fresh standard.
   3. Recalibrate the instrument.
   4. Perform preventative maintenance.
   5. Perform mass calibration and re-tuning the instrument.
   6. Reanalyze all affected samples per attached requirements.
   7. Take measures to eliminate sources of contamination.

2) BLANKS

a. Sources and expected review procedures:
   1. Contaminated reagents – verify reagent sources.

2. Environmental contamination (all sample collection, sample and analysis conditions) – review sampling handling protocols

TABLE 9.0 CONTINUED...

3. Improper or incomplete laboratory and/or field decontamination/cleaning procedures – review cleaning protocols.
4. Contaminated sample containers – verify source and storage conditions.
5. Contaminated source water – verify water sources.

b. Expected corrective actions:

1. Review data with respect to reported contamiation levels. If blank concentrations are near the sample levels, and are above the control criteria, reprocess (re-extract or re-digest) associated samples or resample. If sample concentrations are significantly higher than blanks, or contamination is not detected in the samples, report data.

2. Take measures to eliminate future problems: discard reagents, revise protocols, perform preventative maintenance on the system, adjust the use of interfering chemicals (solvents, fuels, etc.).

3) SPIKES (including Surrogate Spikes and Internal Standard Spikes)

a. Sources and expected review procedures:

1. Error in calculation – review/recheck all calculations.
2. Error in preparing or using spike solutions – review all preps. for proper dilutions, solvents, buffers, etc.
3. Outdated standards – review expiration dates and standard preparation logs.
4. Contamination problems (see Blanks #2).
5. Poor instrument response – determine if preventative maintenance is required.
6. Matrix interferences.

b. Expected Corrective Actions:

1. Take measures to eliminate contamination problems, reprocess if necessary.
2. Perform required maintenance and revise preventative maintenance schedules.
3. Review preparation, calculation and record keeping to determine if additional training or more strict protocols are needed.
4. If none of the sources discussed above are responsible for the problem, the sample must be reprocessed and/or reanalyzed. If reanalysis produces the same result, associated samples should be reported with qualified results. If results are different, all associated samples must be processed for analysis.
5. Internal Standards Only - Reanalyze samples from last acceptable QC check to next acceptable QC check.

4) SYSTEM PERFORMANCE CHECKS

a. Sources and expected review procedures:

1. Pesticides: Poor column performance – replace column.
2. Standard reference materials and QC check samples:
   a. Improper sample preparation or analysis – review all protocols associated with sample preparation and analysis.
   b. Incorrect dilutions or calculations – recheck all calculations.
   c. Contamination (See Blank #2)

b. Expected corrective action:

1. Reanalyze all samples that are effected per method requirements.
2. Reprocess all samples associated with QC check sample or standard reference material (unless the problem is unique to processing of the check sample).
3. Take measures to eliminate sources of contamination.

5) DUPLICATES (including Split Samples)

a. Sources and expected review procedure:

1. Non-representative sample – review sample collection and/or sample processing protocols.
2. Error in calculations – recheck calculations.

3. Contamination problems (See Blanks #2).
4. See Spikes #3.

b. Expected corrective actions:

1. Report data with qualifiers and explanation.
2. Revise sample collection/sample processing protocols to assure a representative sample.
3. Take measures to eliminate contamination problems.
4. Reprocess and reanalyze sample set (if laboratory generated replicate).

6) TITRATIONS

a. Sources and expected review procedures:

1. Error in calculation – review/recheck all calculations.
2. Error in preparing or using titrant and standard solutions – review all preparation and/or analytical logs (including sample preparation) for proper dilutions, solvents, buffers, etc.
3. Outdated standards – review expiration dates and standard preparation logs.
4. Contamination problems (See Blank #2).
5. Non-representative samples – review sample collection and/or sample processing protocols.
6. Indistinct or inconsistent endpoint readings.

b. Expected corrective actions:

1. Take measures to eliminate contamination problems, reprocess if necessary.
2. Review preparation, calculation and record keeping to determine if additional training or more stringent protocols are needed.
3. If replicate analyses are not acceptable, titrate additional aliquots.
4. Reanalyze samples from last acceptable QC check to next acceptable QC check.
5. Train analyst to titrate to consistent endpoint.

TABLE 10.0 MAXIMUM CONTAMINANT LEVELS (MCL)

	MCL(µg/L)
➢ **INORGANIC CONTAMINANTS**	
Arsenic	10
Antimony	6
Barium	2000
Beryllium	4
Cadmium	5
Chromium	100
Copper	1300
Cyanide (as free cyanide)	200
Fluoride	4000
Lead	15
Mercury	2
Nitrate	10,000 (as nitrogen)
Nitrite	1,000 (as nitrogen)
Total Nitrite+Nitrate	10,000 (as nitrogen)
Selenium	50
Thallium	2

➢ **MICROBIOLOGICAL** Total Coliforms (including Fecal Coliform and *E.coli*) MCL = zero

➢ ORGANIC CONTAMINANTS	MCL (µg/L)		MCL (µg/L)
Benzene	5	1,1,2-Trichloroethane	5
Vinyl chloride	2	1,2,4-Trichlorobenzene	70
Carbon tetrachloride	5	Chlorobenzene	100
1,2-Dichloroethane	5	Alachlor	2
Trichloroethene	5	Chlordane	2
Dibromochloropropane	0.2	Heptachlor	0.4
1,2-Dichloropropane	5	Heptachlor epoxide	0.2
Ehtylene dibromide	0.05	Pentachlorophenol	1
Tetrachloroethene	5	Polychlorinated biphenyls (PCBs)	0.5
Methylene chloride	5	Toxaphene	3
1,1-Dichloroethylene	7	Atrazine	3
1,1,1-Trichlorethane	200	2,4-D	70
1,4-Dichlorobenzene	75	Lindane	0.2
1,2-Dichlorobenzene	600	Methoxychlor	40
cis-1,2-Dichlorobenzene	70	2,4,5-TP	50
trans-1,2-Dichlorobenzene	100	Dalapon	200
Ethylbenzene	700	Dinoseb	7
Styrene	100	Endrin	2
Toluene	1000	Picloram	500
Xylenes (Total)	10,000	Simazine	4
Benzo(a)pyrene (PAHs)	0.2		
Total Trihalomethanes (Bromoform, Chloroform, Bromodichloromethane, Chlorodibromomethane	100		

FIGURES

FIGURE 1.0 BRIGHTON ANALYTICAL ORGANIZATIONAL CHART

PRESIDENT - COLLEEN TOPOLSKI

LABORATORY DIRECTOR - WILLIAM TOPOLSKI

QUALITY ASSURANCE MANAGER - MICHELLE MEISEL

LABORATORY SUPPORT & SAMPLE RECEIPT– DEBBIE HOFFNER

CUSTOMER SERVICE/PROGRAM MANAGEMENT - JEFF TOPOLSKI

ORGANICS DEPARTMENT - CINDY WILLIAMS – SUPERVISOR
ANALYSTS: RENATA GOROWICZ & BERNARD YOUNG
EXTRACTIONS: MIKE BOYER

INORGANICS DEPARTMENT - GARY WAGNER – SUPERVISOR
ANALYSTS: KAT WALTERS
DIGESTIONS/MICROBIOLOGY: LAURIE SNEED
WET CHEMISTRY: RANDY MANN

FIGURE 2.0 DAILY BALANCE MONITORING

BALANCE MONITORING

DAILY BALANCE MONITORING INSTRUCTIONS:

1. Each balance is checked daily or immediately before use with NIST Class S metric weights or better.
2. Enter the measured value into the log below.
3. Check the results against the criteria listed* and enter the analyst's initials & date checked.

Balance Model: **Balance Weighing Capacity:**

Location : **Acceptance Criteria: + 0.05 g**

Date	Time	NIST Class S Weight Used	Measured Weight	Initials	Acceptable Y or N

*** If results fail the acceptance criteria listed, notify the Quality Assurance Manager immediately.**

FIGURE 3.0 EXAMPLE OF REFRIGERATOR/FREEZER DAILY RECORD OF TEMPERATURE FORM

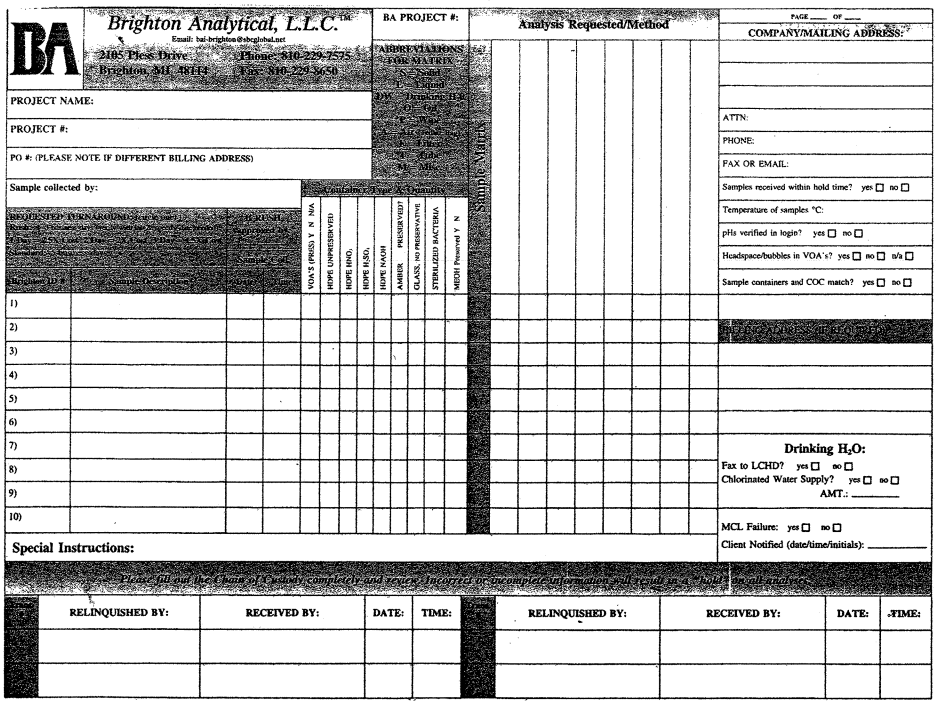
BA-08 (BACK)
CERT #12427
TEMP: 4°C
Corr. Fact.- 0.5

DAILY THERMOMETER TEMPERATURE RECORD

Dept. **WALK-IN #1** Temperature Range **2°C** To **6°C** Year **2014**

MONTH	JANUARY		FEBRUARY		MARCH		APRIL		MAY		JUNE	
	RECORD	INITIAL	RECORD	INITIAL	RECORD	INITIAL	RECORD	INITIAL	RECORD	INITIAL	RECORD	INITIAL
DAY 1												
2												
3												
4												
5												
6												
7												
8												
9												
10												

FIGURE 4.0 Chain-Of-Custody Form



Brighton Analytical, L.L.C.
Email: bal-brighton@sbcglobal.net
2105 Pless Drive Phone: 810-229-7575
Brighton, MI 48114 Fax: 810-229-3650

BA PROJECT #:

Analysis Requested/Method

PAGE ___ OF ___

COMPANY/MAILING ADDRESS:

PROJECT NAME:

PROJECT #:

PO #: (PLEASE NOTE IF DIFFERENT BILLING ADDRESS)

Sample collected by:

ATTN:

PHONE:

FAX OR EMAIL:

Samples received within hold time? yes ☐ no ☐

Temperature of samples °C:

pHs verified in login? yes ☐ no ☐

Headspace/bubbles in VOA's? yes ☐ no ☐ n/a ☐

Sample containers and COC match? yes ☐ no ☐

Container Type & Quantity

Sample Matrix

Sample ID #	VOA'S (PRES) Y N N/A	HDPE UNPRESERVED	HDPE HNO3	HDPE H2SO4	HDPE NAOH	AMBER PRESERVED?	GLASS, NO PRESERVATIVE	STERILIZED BACTERIA	MEOH Preserved Y N
1)									
2)									
3)									
4)									
5)									
6)									
7)									
8)									
9)									
10)									

Drinking H_2O:
Fax to LCHD? yes ☐ no ☐
Chlorinated Water Supply? yes ☐ no ☐
AMT.: _____

MCL Failure: yes ☐ no ☐
Client Notified (date/time/initials): _____

Special Instructions:

Please fill out the Chain of Custody completely and neatly. Incorrect or incomplete information will result in a short turn-around time.

RELINQUISHED BY:	RECEIVED BY:	DATE:	TIME:	RELINQUISHED BY:	RECEIVED BY:	DATE:	TIME:

FIGURE 5.0 PROJECT MODIFICATION REPORT

BA PROJECT #: _____ **CLIENT:**_____ **INITIATED BY:**_____ **DATE:**_____

____**ADD SAMPLES** ____**DELETE SAMPLE(S)** ____**ADD ANALYSIS**
____**DELETE ANALYSIS** ____**SUBCONTRACT** ____**DROP PROJECT**
____**OTHER-**_____ ____**CHANGE DUE DATE**

COMMENTS:_____
_____
_____
_____

PRICING: _____
_____

DEPARTMENTS:

LOG-IN ____ **% SOLIDS** ____

METALS____ **WETCHEM** ____ **DIGESTION** ____

GC ____ **GC/MS** ____ **EXTRACTIONS**____

FIGURE 6.0 STANDARD PREPARATION LOG

Standard Name: _____ Analyst&Date: _____ STD ID# _____

SOLVENT INFORMATION		STANDARD INFORMATION	
Solvent:	_____	Date Opened:	_____
Source:	_____	Source:	_____
Lot No.:		Lot No.:	

Final Volume of Std: Date Std Expires:

	Compound(s)	Source/Lot Number	Conc. of parent soln. (µg/mL)	Vol or Wt (mg) used	Final Conc. µg/mL
1.					
2.					
3.					
4.					

Working Standard Dilutions

Volume of Standard: _____ Solvent: _____
Final Vol of Working Std: _____ Source of Solvent:
Final Concentration : _____ Lot # of Solvent:

FIGURE 7.0 CORRECTIVE ACTION FORM CA Form: _____

Initiated By: _____ **Date:** _____ **Date CA Due:** _____

Assigned to: _____ **Analysis:** _____ **Date Run(if applicable):** _____

Sample Number (if applicable): _____

PROBLEM

**Contaminated Method Blank ( ) Method Standard Recovery ( ) Spike Recovery ( ) Surrogate Recovery ( )
Internal Standard Recovery ( ) Validity of Curve ( ) Precision of Duplicates ( ) Continuing Calibration Std. ( )
Secondary Ref. Matl.( )**

OTHER (specify): _____

Probable Cause(s): _____

Action Proposed/Taken: _____

Problem Resolved (if no, indicate action to take):
( ) YES ( ) NO _____

Followup (Date): _____

FIGURE 8.0 CLIENT COMPLAINT CORRECTIVE ACTION FORM

Initiated By: _____ **Date:** _____ **Date CA Due:** _____ **CA NO.:** _____

Assigned to: _____ **Analysis:** _____ **Date Run(if applicable):** _____

Sample Number (if applicable): _____

PROBLEM

(specify): _____

Probable Cause(s): _____

Action Proposed/Taken: _____

Problem Resolved (if no, indicate action to take):
( ) YES ( ) NO _____

Followup (Date): _____

FIGURE 9.0

INTERNAL AUDIT CHECKLISTS

(Examples of various methods- complete list can be located in the Quality Assurance Office)

Brighton Analytical L.L.C.

ANNUAL INTERNAL AUDIT
SAMPLE RECEIPT

	YES	NO	Comments
Sample Receipt and Handling			
° Written sample acceptance policy available:			
° COC completely and properly filled out, including but not limited to, Sample ID, Location of collection, date of collection, time of collection, collectors name, preservation and bottle types, sample types, analysis, signature of client releasing samples to laboratory:			
° Any problems, damage, hold time issues etc. recorded on the COC:			
° Temperature and preservation properly verified upon receipt and recorded on COC:			
° Labels durable and water resistant:			
° Each sample container uniquely ID:			
° Samples being processed in timely manner (if not-properly stored at 4°C)			
° Contact with client being recorded on COC:			
° "RUSH" analysis and short hold time analysis being properly communicated to the laboratory staff:			
° Samples being properly stored:			
° Methods requested on the COC appropriate for the tests being requested:			
° Test and calibration methods, including methods for sampling, meet the needs of the customer and appropriatefor the tests and/or calibrations it undertakes.			
° Use of appropriate sample containers:			
° Sufficient sample volume to perform the necessary tests:			
° Samples which show signs of damage, contamination or inadequate preservation being documented completely and thoroughly on the COC:			
° Qualification of samples that do not meet any of the requirements above:			
° All correspondance with client during sample receipt recorded on COC or attached:			
° Sample receipt recording client, project name, date/time of laboratory receipt, unique sample ID, initials of person making entries, lab ID placed on sample containers:			
° Field ID code linkied to the lab ID code in sample receipt log:			
° Any comments resulting from inspection of sample rejection linked to lab ID code:			
° Samples stored away from all standards, reagents and food:			

N/A = Not Applicable

Auditor/Date: _____

INTAUDITSAMPLEREC2013

Brighton Analytical L.L.C.

ANNUAL INTERNAL AUDIT

SAMPLE LOGIN/DATA REVIEW/REPORT GENERATION/CORRECTIVE ACTIONS

	YES	NO	Comments
SAMPLE LOGIN			
° Samples being logged in to the computer after receipt:			
° Any qualifications noted during sample receipt being added to report at time of login:			
° When client does not request specific methods, are appropriate methods that have published in either national standards or equivalent:			
° Is the customer being informed as to the method chosen:			
° Does the laboratory confirm that it can properly operate standard methods before introducing the tests or calibrations:			
° If the standard method is changed, the confirmation with client is repeated:			
° Laboratory informs client when the method proposed by the customer is considered inappropriate or out of date:			
° All documentation, such as memos, chains of custody, or transmittal forms, e.g. facsimiles or emails, are retained by the laboratory:			
° Complete chain of custody form maintained:			
DATA REVIEW			
° All data being reviewed before data entry:			
° Corrective actions being implemented and followed up with out-of-control data:			
° Data packages complete with all quality control including curve data, blanks, sample results, continuing calibrations, matrix spikes/duplicates, etc:			
° Data signed and dated by reviewer before being released to data entry:			
° Calculations and data transfers checked in a systematic manner:			
° Data signed and dated by reviewer:			
DATA ENTRY/REPORT GENERATION			
° Data being entered from the analyst's raw data sheets:			
° Final reports being generated in a timely manner:			
° Analysis data is appropriately qualified on the final report:			
° All qualifiers, from sample receipt to analysis, present on final report:			
° Final report generation and review completed, signed and dated:			
° All corrective actions generated from sample submission to report generation addressed and complete before data released to client:			
° Any quotes or correspondance relating to test methods, etc .followed and completed to satisfy the clients needs/specifications:			
° The final reports contains laboratory address, name of customer, method, dates of receipt, report date, sample date/time, results, etc.:			

Auditor/Date: _____ N/A = Not Applicable

INTAUDITSLOGIN-REV-REPORTS2013

QUALITY CONTROL CHECKLIST FOR MICROBIOLOGY

INTERNAL AUDIT CHECKLIST
MICROBIOLOGY
METHOD: ATP D05-0035

REVIEWED BY/DATE: _____
ANALYST: _____

Y/N: Enter Yes if the QC meets the criteria, No if the QC fails the criteria.

#	QC Check	Minimum Frequency	Y	N	Comments/ Corrective Actions
1	Adequacy of sterilization assessed	Each autoclave cycle?			
2	Automatic timing mechanism of the autoclave checked to ensure accuracy	Quarterly?			
3	Sample containers	Wide mouth containing sodium thiosulfate? At least 120-mL to allow 1 inch head space?			
4	Sample containers	One container selected from each batch and sterility confirmed by adding approximately 25mL of sterile non-selective broth? Checked at 24 and 48 hours of growth and results recorded?			
5	Sodium thiosulfate	Provided in bottles used for chlorinated samples?			
6	Contaminated Materials Autoclaved	Minimum 30 minutes?			
7	Permanent records	Kept for commercially prepared media including date received, type of medium, lot number and pH verification?			
8	Colitag Medium	Each lot checked for autofluorescence?			
9	Incubators	Maintained at 35±0.5°C?			
10	Incubation Time Period	Documented for the sterility checks for each lot of non-selective broth?			

NT AUD WORKSHEET ATPD05-0035.XLS

INTERNAL AUDIT CHECKLIST

MICROBIOLOGY

METHOD: ATP D05-0035 (MODIFIED COLITAG METHOD)

			COMMENTS
1.	Daily incubator temperatures being recorded at least 4 housrs apart?	Y N	
2.	Autoclave records indicate the total sterilization cycle time (not the total time of the acutoclave cycle)?	Y N	
3.	Using spore strips or ampules at least monthly to confirm sterility?	Y N	
4.	Verification of the 100-mL calibration mark of sample containers per lot and documented?	Y N	
5.	Performing sterility checks for each batch of sample containers including documentation?	Y N	
6.	Performing the complete total coliform procedure at least quarterly with a known *E. coli* positive control?	Y N	
7.	Recording the date received, type of media, lot number, verifying the pH of each lot of non-selective broth used in the sterility check for the sample containers?	Y N	
8.	Checking each lot of non-selective broght (used in the sterility check for the sample containers) with positive culture controls at 24 and 48 hours? **(REPEAT DEFICIENCY IN 2009)**	Y N	
9.	Documenting the incubation time period for the sterility checks for each lot of non-selective broth?	Y N	
10.	Standard operating procedure referencing ccorrect media/procedure ATP D05-0035 Modified Colitag method?	Y N	
11.	All microbiology waste being autoclaved including Quanti-Trays?	Y N	
12.	Correct correction factor being used when calibrating with the NIST thermometers (this is the closest correction factor at the point of use of the thermometer)?	Y N	
13.	Performing **Quarterly** automatic timer mechanism checks by documenting the automatic timer checks for 30 minutes sterilization runs and total run time of sterilization cycle?	Y N	
14.	For commercially prepared media, analyst recoding date received, type of medium, lot number and results of pH verification (if applicable) for each lot of tryptic soy broth?	Y N	
15.	Performing and documenting a positive control and a sterility check for each lot of commercially prepared tryptic soy broth?	Y N	
16.	Are blinds analyzed two times per year? When a blind result fails is a new standard analyzed after taking corrective action? (One acceptable blind in a calendar year required)	Y N	
17.	Following correct procedures for all data changes, i.e., single line, date & initials?	Y N	
18.	Training records up to date for analyst? (e.g. MDL, annual integrity training, annual QAPP review, etc.)	Y N	

Analyst: _____

Auditor/Date: _____

INT AUD FINDINGS ATP D05-0035.XLS

INTERNAL AUDIT CHECKLIST

AMMONIA
METHOD: SM 4500 NH3-G

			COMMENTS
1.	Are samples stored at ≤6°C prior to analysis and preserved at pH <2 using sulfuric acid?	Y N	
2.	Are the samples analyzed within the 28 day hold time (preserved at pH <2 and ≤6°C)?	Y N	
3.	Is absorbance measured at wavelentgth 630?	Y N	
4.	Is the spectrophotometer calibrated with at least 3 standards and a blank? Is the calibration curve acceptable (0.995 or better)?	Y N	
5.	Is the calibration curve verified with a quality control sample (a secondary standard independent from the standards used for curve? Is the quality control standard check within ±10%?	Y N	
6.	If quality control standard not within ±10%, is it reanalyzed? If fails a second time is the instrument re-calibrated and verified?	Y N	
7.	Samples above the calibration curve diluted and re-analyzed?	Y N	
8.	Concentration value of sample directly read from prepared standard curve?	Y N	
9.	Is a blank run with each sample batch and processed in the same manner as the samples?	Y N	
10.	Is the correct criteria applied to the known standards (+/-10%)?	Y N	
11.	Are matrix spike/matrix spike duplicates analyzed for each batch of samples? A criteria of ±20% or in-house limits applied?	Y N	
12.	Are CCV, MS & MSD standard ID#s being identified on the raw data?		
13.	Are blinds analyzed two times per year? When a blind result fails is a new standard analyzed after taking corrective action?	Y N	
14.	Following correct procedures for all data changes, i.e., single line, date & initials?	Y N	
15.	Training records up to date for analyst? (e.g. MDL, annual integrity training, annual QAPP review, etc.)	Y N	

Analyst: _____

Auditor/Date: _____

INT AUD FINDINGS 4500NH3G.XLS

INTERNAL AUDIT CHECKLIST

PHENOLICS

METHOD: EPA 420.1

			COMMENTS
1.	Are samples stored at ≤6°C prior to analysis and preserved at pH <2 using sulfuric acid?	Y N	
2.	Are the samples analyzed within the 28 day hold time (preserved at pH <2 and ≤6°C)?	Y N	
3.	Are samples acidified to a pH of less than 2.0 with H_2SO_4 therefore eliminating interferences from sulfur compounds?	Y N	
4.	Is a blank run with each sample batch and distilled in the same manner as the samples? (Batch ≤20 samples)	Y N	
5.	Is a matrix spike/matrix spike duplicate run with each sample batch and distilled in the sample manner as the samples? (Batch ≤20 samples)	Y N	
6.	Calibration being verified with a second source reference standard that is different than the standard used for calibration?	Y N	
7.	Is absorbance measured at wavelentgth 460nm?	Y N	
8.	Samples above the calibration curve diluted and re-analyzed?	Y N	
9.	Is the correct criteria applied to the known standards (+/-10%)?	Y N	
10.	Are blinds analyzed two times per year? When a blind result fails is a new standard analyzed after taking corrective action?	Y N	
11.	Following correct procedures for all data changes, i.e., single line, date & initials?	Y N	
12.	Training records up to date for analyst? (e.g. MDL, annual integrity training, annual QAPP review, etc.)	Y N	

Analyst: _____

Auditor/Date: _____

INT AUD FINDINGS 420-1.XLS

INTERNAL AUDIT CHECKLIST
TOTAL KJELDAHL NITROGEN
METHOD: SM 4500-NorgB

			COMMENTS
1.	Are samples stored at ≤6°C prior to analysis and preserved at pH <2 using sulfuric acid?	Y N	
2.	Are the samples analyzed within the 28 day hold time (preserved at pH <2 and ≤6°C)?	Y N	
3.	Instrument calibrated with 5 standards (0.1, 0.25, 0.5, 2.0 & 5.0-ppm) established curve with a correlation coefficient of 0.995 or better?	Y N	
4.	Calibration curve is verified with an independent external reference standard within ±10%? If not within acceptable limits, analysis terminated and re-calibrated? If recalibrated, verified with external reference standard?	Y N	
5.	Linear calibration range verified every 6 months or as needed (when a significant change in instrument response is observed)? Verification of linearity employs a minimum of a blank and 3 standards?	Y N	
6.	Quality control sample (independent secondary reference standard) analyzed quarterly and within ±10%?	Y N	
7.	A method blank and LCS (method standard) is analyzed with each batch of sample (batch ≤20 samples)? LCS within ±10%?	Y N	
8.	Method blank analyzed before samples and below the detection limit? Detectable blanks are re-analyzed and if still positive, either increase the detection limit or re-digestion of the sample set?	Y N	
9.	Instrument performance check solution (mid range certified standard) and blank analyzed before sample analysis, after every 10th sample and end of the sample run and within ±10%? If IPC fails, corrective action performed and all samples following last acceptable IPC solution reanalyzed?	Y N	
10.	Matrix spike/Matrix spike duplicate analyzed with each batch of samples (≤20 samples) with ±10%? If outside range, reanalyzed and fails again, deemed matrix or solution relate and flagged and reported?	Y N	
11.	Following correct procedures for all data changes, i.e., single line, date & initials?	Y N	
12.	Training records up to date for analyst? (e.g. MDL, annual integrity training, annual QAPP review, etc.)	Y N	

Analyst: _____

Auditor/Date: _____

INT AUD FINDINGS 4500-NorgB.XLS

INTERNAL AUDIT CHECKLIST

CHEMICAL OXYGEN DEMAND
METHOD: EPA 410.4

			COMMENTS
1.	Are samples stored at ≤6°C prior to analysis and preserved at pH <2 using sulfuric acid?	Y N	
2.	Are the samples analyzed within the 28 day hold time (preserved at pH <2 and ≤6°C)?	Y N	
3.	Instrument calibrated with 4 standards (10, 50, 100 & 150ppm) and method blank to establish a linear calibration range? Results do not exceed ±10% or linearity is re-established? Linear calibration Range performed every 6 months or as needed?	Y N	
4.	Zero the instrument to a method blank? Check with a known ERA standard (within ±10%) before analysis?	Y N	
5.	Hot block digestor verified at 150C and recorded in logbook?	Y N	
6.	Quality control sample analyzed quarterly and within ±10%?	Y N	
7.	Limit of detection performed annually to verify the MDL. Analyte is qualitatively idendified at a concentration 2-3x the MDL. An LOD of 6-ppm is used?	Y N	
8.	A method blank and LCS (method standard) is analyzed with each batch of sample (batch ≤20 samples)? LCS within ±10%?	Y N	
9.	Method blank analyzed before samples and below the detection limit? Detectable blanks are re-analyzed and if still positive, either increase the detection limit or re-digestion of the sample set?	Y N	
10.	Instrument performance check solution (mid range certified standard) and blank analyzed before sample analysis, after every 10th sample and end of the sample run and within ±10%? If IPC fails, corrective action performed and all samples following last acceptable IPC solution reanalyzed?	Y N	
11.	Matrix spike/Matrix spike duplicate analyzed with each batch of samples (≤20 samples) with ±10%? If outside range, reanalyzed and fails again, deemed matrix or solution relate and flagged and reported?	Y N	
12.	Following correct procedures for all data changes, i.e., single line, date & initials?	Y N	
13.	Training records up to date for analyst? (e.g. MDL, annual integrity training, annual QAPP review, etc.)	Y N	

Analyst: _____

Auditor/Date: _____

INT AUD FINDINGS 410-4.XLS

INTERNAL AUDIT CHECKLIST
BIOLOGICAL OXYGEN DEMAND
METHOD: SM 5210B

			COMMENTS
1.	Is a blank run with each sample batch and processed in the same manner as the samples? Is corrective action taken if the method blank is above the LOD?	Y N	
2.	Is a replicate run after the analysis of 20 samples? Are quality control limits for replicates calculated?	Y N	
3.	Are quality control limits used to assess replicate performance each time replicates are analyzed?	Y N	
4.	When QC limits for standards, replicates or blanks exceeded is corrective action taken?	Y N	
5.	Is a known standard (GGA) analyzed after 20 samples (±10%)?	Y N	
6.	Is the GGA standard analyzed at a 2% dilution (6mL to 300mL) using a concentration that yields 3mg/L glucose and 3mg/L glutamic acid in the GGA test bottle?	Y N	
7.	Do GGA results meet the 198±30.5mg/L BOD standard? Multiple GGA standards cannot be averaged.	Y N	
8.	Do all samples, standards and seed controls used to calculate results meet the depletion criteria?	Y N	
9.	If criteria are not met are data excluded from calculations or qualified if there are no acceptable dilutions to use?	Y N	
10.	Do dilution water blanks meet the depletion limit of <0.2 mg/L DO?	Y N	
11.	Are blinds analyzed two times per year? When a blind result fails is a new standard analyzed after taking corrective action?	Y N	
12.	Sample results traceable to analyst, date collected, method used including raw data, calculations, results and final report?	Y N	
13.	Are clear records of replicates and associated control limits available and current?	Y N	
14.	Are records associated with blinds and reference samples available?	Y N	
15.	Are records of corrective actions taken in response to QC failures present and available?	Y N	
16.	Are BOD samples set up within 48 hours of collection? Samples brought to room temperature before analysis?	Y N	
17.	Buffer water (dilutions) prepared daily?	Y N	
18.	Internal DO measurement below 9.0?	Y N	
19.	Samples checked for residual chlorine? If residual chlorine found, sample neutralized?	Y N	
20.	Each batch of samples has a duplicate?	Y N	
21.	Blank (dilution water) with each batch of samples?	Y N	

INT AUD FINDINGS 5210B.XLS

22.	pH checked in login and before BOD set-up? pH adjusted to 6.5-7.5 if not in pH 6.0-8.5 initially?	Y N	
23.	If pH adjustment is done, the amount of acid or base used limited to ≤0.5% of sample volume?	Y N	
24.	Samples over the 100% DO saturation value identified and treated for super saturation?	Y N	
25.	The DO meter calibrated each analysis day?	Y N	
26.	Incubator maintain samples at 20C±0.5C during 5 day test?	Y N	
27.	Seed source Polyseed and are all samples seeded? Seed prepared by adding 1 seed capsule to 500mL?	Y N	
28.	Analyst prepares a minimum of 3 dilutions to meet the depletion criteria?	Y N	
29.	Are BOD values properly calculated for all samples?	Y N	
30.	Following correct procedures for all data changes, i.e., single line, date & initials?	Y N	
31.	Training records up to date for analyst? (e.g. MDL, annual integrity training, annual QAPP review, etc.)	Y N	

Analyst: _____

Auditor/Date: _____

INTERNAL AUDIT CHECKLIST

PHOSPHORUS

METHOD: SM 4500 P-E

			COMMENTS
1.	Are samples stored at ≤6°C prior to analysis and preserved at pH <2 using sulfuric acid?	Y N	
2.	Are the samples analyzed within the 28 day hold time (preserved at pH <2 and ≤6°C)?	Y N	
3.	Samples warmed to room temperature before beginning digestion?	Y N	
4.	Vial capped tightly and shaken, then placed in the pre-heated block digester at 110°C for 30 minutes?	Y N	
5.	Is the sample cooled for 10 minutes, 2 mL of 1.54N NaOH solution and 1 packet of PhosVer3 Phosphate Reagent added to each vial, and then capped and shaken?	Y N	
6.	Are turbid samples centrifuged?	Y N	
7.	Sample absorbance measured between 2 and 8 minutes after phosver4 pillow packet is added? No longer than 15 minutes?	Y N	
8.	Is the spectrophotometer calibrated with at least 3 standards and a blank? Is the calibration curve acceptable (0.995 or better)?	Y N	
9.	Is absorbance measured at wavelentgth 890?	Y N	
10.	Samples above the calibration curve diluted and re-analyzed?	Y N	
11.	Concentration value of sample directly read from prepared standard curve?	Y N	
12.	Is a blank run with each sample batch and processed in the same manner as the samples?	Y N	
13.	Are matrix spike/matrix spike duplicates analyzed for each batch of samples? A criteria of ±20% or in-house limits applied?		
14.	Is the correct criteria applied to the known standards (+/-10%)?	Y N	
15.	Are blinds analyzed two times per year? When a blind result fails is a new standard analyzed after taking corrective action?	Y N	
16.	Following correct procedures for all data changes, i.e., single line, date & initials?	Y N	
17.	Training records up to date for analyst? (e.g. MDL, annual integrity training, annual QAPP review, etc.)	Y N	

Analyst: _____

Auditor/Date: _____

INT AUD FINDINGS 4500PE.XLS

A complete collection of internal audit forms can be located in the Quality Assurance Office.

OTHER MISCELLANEOUS FORMS (Located in the Quality Assurance Office):

Quality Control Checklists for:

Semi-Volatiles Analysis
Volatile Analysis
Herbicides
PCB/Pesticides
Volatile Drinking Water
Mercury
Metal Analysis
Ion Chromatography
Cyanide
Total Organic Carbon
Phenolics
Nitrogen, Kjeldahl (TKN)

APPENDIX A
LIST OF MOST COMMONLY REQUESTED METHODS AT BRIGHTON ANALYTICAL
ENVIRONMENTAL ANALYSES (*Indicates NELAC Certified Analysis)

SOIL AND WATER

Acidity – EPA 305.1 or SM 2310
Alkalinity – EPA 310.1 or SM 2320B
*Base/Neutral & Acid Extractables
GC/MS Analysis of Semi-Volatile Organics, EPA 625 or EPA 8270
*Biological Oxygen Demand (BOD) – EPA 405.1 or SM5210B
*Chemical Oxygen Demand (COD) – EPA 410.4
*Chlorinated Herbicides – EPA 615 or EPA 8151
Chlorinated Hydrocarbons – EPA 612 or EPA 8121
Chlorine, Total Residual – EPA 330.5
Coliform (Total & Fecal) – SM 9221, SM 9221 Modified, SM 9222, SM 9222 Modified
Color – EPA110.2 or SM 2120B
*Conductivity (Specific Conductance) – EPA 120.1
*Cyanide, Amenable to Cl^- -- EPA 335.4 or EPA 9012
*Cyanide, Total – EPA 335.4 OR EPA 9012
Cyanide, Available – OIA 1677
Diesel Range Organics (DRO) – EPA 8015M or 8270M
Extractable Organic Halides (EOX) – EPA 9023
*Flashpoint (Ignitibility) – EPA 1010
Formaldehyde – EPA 8315
Gasoline Range Organics (GRO) – EPA 8015M or EPA 8260
Glycols – EPA 8015M
*Hardness (by calculation) – SM 2340B
Hexavalent Chromium (Cr-VI) –(EPA 3060/7195-Prep Methods) Analyzed by EPA 6010.
*Ion Chromatography – EPA 300.0
Including Chloride, Fluoride, Nitrate, Nitrite, Sulfate
Metals –
Inductively Coupled Plasma (ICP) – EPA 200.7 or EPA 6010.
*ICP-Mass Spectroscopy – EPA 200.8 or EPA 6020.
Metals Scan:
Aluminum (Al), Antimony (Sb), Arsenic (As), Barium (Ba), Beryllium (Be), Boron (B), Cadmium (Cd), Calcium (Ca), Chromium (Cr), Cobalt (Co), Copper (Cu), Iron (Fe), Lead (Pb), Lithium (Li), Magnesium (Mg), Manganese (Mn), Molybdenum (Mo), Nickel (Ni), Potassium (K), Selenium (Se), Silver (Ag), Sodium (Na), Strontium (Sr), Thallium (Tl), Tin (Sn), Titanium (Ti), Vanadium (V), and Zinc (Zn).

10 Michigan Metals: (DEQ, MDNR) *Arsenic, Barium, Cadmium, Chromium, Copper, Lead, Mercury, Selenium, Silver, Zinc.*

RCRA Metals: *Arsenic, Barium, Cadmium, Chromium, Lead, Mercury, Selenium, Silver.*

Priority Pollutant Metals: *Antimony, Arsenic, Beryllium, Cadmium, Chromium, Copper, Lead, Mercury, Nickel, Selenium, Silver, Thallium, and Zinc.*

*Mercury – (Hg) EPA 245.1 or EPA 7470 or EPA 7471
*Low Level Mercury - EPA 1631E
Methylene Blue Active Substances (MBAS - Surfactants) – EPA 425.1 or SM5540C
*Nitrogen, Kjeldahl – EPA 351.2 or SM4500-NorgB
*Nitrogen, Ammonia – EPA 350.3

*Nitrogen, Nitrate (NO_3) – EPA 300.0
*Nitrogen, Nitrite (NO_2) – EPA 300.0
Odor Threshold – EPA 140.1
Oil & Grease, Total Recoverable – EPA 413.1 or EPA 1664 (Gravimetric) & EPA 418.1 (Infrared)
*Organochlorine Pesticides – EPA 608 or EPA 8081
Organophosphorus Herbicides – EPA 8141
Paint Filter Test – EPA 9095
Percent Solid – ASTM D 2216
Percent Water – Karl Fischer Titration – ASTM E 203
Moisture Content – ASTM D 2216
*pH (Corrosivity) – EPA 150.1 or SM4500H+B or 9040B or 9041 or 9045
Phenols – EPA 604 or 624 or 8270 or 8041
*Phenolics, Total – EPA 420.1
*Phosphorus, All Forms – EPA 365.2 or SM4500-PE
Phthalate Esters – EPA 606 or EPA 624 or EPA 8270 or EPA 8061
*Polychlorinated Biphenyls (PCBs) – EPA 608 or EPA 8082
*Polynuclear Aromatic Hydrocarbons (PAHs) – EPA 625 or EPA 8270
Reactivity --
    Cyanide – EPA SW846 Sect. 7.3.3.2 or EPA 9010
    Sulfide – EPA SW846 Sect. 7.3.4.2 or EPA 9030
Solids – Residue
    Filterable (Total Dissolved Solids) – EPA 160.1 or SM 2540C
    Non- filterable (Total Suspended Solids) – EPA 160.2 or SM2540D
    Settleable – SM 2540
    Total (Percent Solid) – EPA 160.3 or ASTM D-2216
    Volatile – EPA 160.4 or SM 2540E
Specific Gravity – ASTM D-70
Sulfide – EPA 376.1 or EPA 9030 or SM4500-S2F
Sulfite – EPA 377.1
Temperature (field parameter) – EPA 170.1
*Total Organic Carbon (TOC) – EPA 415.1 or EPA 9060 or SM5310B
Total Organic Halide (TOX) – EPA 9020
Total Petroleum Hydrocarbons (TPH) – EPA 418.1 or EPA 8015M or EPA 8100

Turbidity – EPA 180.1
Volatile Organics --
    Purgeable Aromatics – EPA 602 or EPA 8020 or EPA 8260 (Mass Spectrometry Only)
    *Purgeable Halocarbons - EPA 8260
    *Purgeable Organics – EPA 8260
    Purgeable Petroleum Hydrocarbons – EPA 8015M

WASTE CHARACTERIZATION

State Regulated Parameters
Michigan Department of Environmental Quality
Organics
    Volatile Organics – EPA 8260
    Semi-Volatile Organics – EPA 8270
    Polynuclear Aromatic Hydrocarbons (PAHs or PNAs) – EPA 8270
    Organochlorine Pesticides – EPA 8081
    Polychlorinated Biphenyls (PCBs) – EPA 8082
Inorganics
    10 Michigan Metals: (DEQ, MDNR) *Arsenic, Barium, Cadmium, Chromium, Copper, Lead, Mercury, Selenium, Silver, Zinc.*
    - Inductively Coupled Plasma (EPA 200.7) and/or ICP-Mass Spectroscopy (EPA 200.8)

Mercury – EPA 7470 or EPA 7471

Federal Regulated Parameters

Toxicity Characteristic Leaching Procedure (TCLP) – EPA 1311 or Synthetic Precipitation Leaching Procedure (SPLP) – EPA 1312

Volatile Organics – *Benzene, Carbon tetrachloride, Chlorobenzene, Chloroform, 1,2-Dichloroethane, 1,1-Dichloroethene, Methyl ethyl ketone (MEK), Tetrachloroethene, Trichloroethene, Vinyl chloride.*

Semi-Volatile Organics – *Cresols (o-, m-, & p-Methylphenol), 1,4-Dichlorobenzene, 2,4-Dinitrotoluene, Hexachlorobenzene, Hexachlorobutadiene, Hexachloroethante, Nitrobenzene, Pentachlorophenol, Pyridine, 2,4,5-Trichlorophenol, 2,4,6-Trichlorophenol.*

Pesticides – *Chlordane, Endrin, Heptachlor, Heptachlor epoxide, Lindane, Methoxychlor, Toxaphene.*

Herbicides – *2,4-D and Silvex (2,4,5-TP).*

Metals – *Arsenic, Barium, Cadmium, Chromium, Copper, Lead, Mercury, Selenium, Silver, Zinc.*

Corrosivity (pH) – SM9040B or SW846 9040B or 9045
Ignitibility (Flashpoint) – EPA 1010
Reactivity—
Cyanide – EPA SW846 Sect. 7.3.3.2 or EPA 9010
Sulfide – EPA SW846 Sect. 7.3.4.2 or EPA 9030

DRINKING WATER

Volatile Organic Compounds – EPA 524.2
Trihalomethanes – EPA 524.2 *Bromoform, Chloroform, Bromodichloromethane, Chlorodibromomethane*
EDB (*Ethylene dibromide*) and DBCP (*1,2-Dibromo-3-chloropropane*)– EPA 504.1
Chlorinated Pesticides – EPA 508 – *Aldrin, Chlordane, Dieldrin, Endrin, Heptachlor, Heptachlor epoxide, Hexachlorobenzene, Hexachlorocyclopentadiene, Lindane (gamma-BHC), Methoxychlor, Propachlor, Toxaphene, Trifluralin.* (Subcontracted to State Lab)
Chlorinated Herbicides – EPA 515.1 – *2,4-D, Silvex (2,4,5-TP), 2,4,5-T, Dalapon, Dinoseb, Dicamba, Pentachlorophenol, Picloram, Aciflurofen.*
(Subcontracted to State Lab)
Coliforms (Total & *E.coli*) – SM 9223
Organophosphorus Pesticides – EPA 507 – *Atrazine, Alachlor, Simazine* (Subcontracted to State Lab)
Metals – EPA 200.8 – *Antimony, Arsenic, Barium, Beryllium, Boron, Cadmium, Chromium, Copper, Lead, Manganese, Molybdenum, Nickel, Selenium, Thallium, Zinc.*
Mercury – EPA 245.1
Inorganics
Alkalinity – SM 2320B
Chloride, Fluoride, Nitrate, Nitrite, Sulfate – EPA 300.0
Conductivity (Specific Conductance) – EPA 120.1
Hardness – EPA 130.2
PCBs as Decachlorobiphenyl – EPA 508A (Subcontracted to State Lab)
pH – EPA 150.1 or SM9040B
Total Cyanide – EPA 335.4
Total Organic Carbon – SM5310B

APPENDIX B
DRINKING WATER BACTERIA SAMPLING PROCEDURES

1. Wash hands thoroughly, do not open sample bottle until you are ready to proceed. Sample results are dependent on proper sampling technique.

2. Sample must be taken from a tap that is representative of the water distribution system, preferably from the sample tap located at or near the water pressure tank. If the pressure tank is not accessible, the sample will be collected from another water tap that is representative of the drinking water system.

3. Water tap must be free of aerators, strainers, hose attachments, mixing type faucets, and purification devices.

4. The **COLD** water tap must be used and the service line cleared before sampling by running the water for at least two minutes, or until the temperature changes.

5. Do **not** touch the inside of the sample bottle or cap.

6. Do **not** rinse sample container (white pill is a preservative).

7. Sterile sample containers must be filled to the 100-ml line so sample volume is sufficient to perform required test. Leave at least a one inch air space to facilitate mixing of the sample by shaking.

The sample collector is responsible for properly packaging and returning the samples to the laboratory for analysis. Chill and protect from sunlight. All samples collected must be received by the laboratory within twenty-four hours. Upon delivery, the sample collector will relinquish custody of the samples to laboratory personnel.

The following information must be entered on a *Chain of Custody* form in indelible ink:

1. Name of owner/system
2. WSSN/Client ID, if applicable
3. Sample number
4. Sample site location (sample tap, kitchen sink, etc.)
5. Sample type (routine, resample, complaint, etc.)
6. Date of collection
7. Time of collection
8. Disinfectant residual
9. Name of sampler/organization
10. Transport/relinquished by information

*For additional testing (arsenic, nitrate, etc.), fill sample bottles after bacteria collection is completed.

BACTERIA SAMPLES NOT ACCEPTED ON FRIDAYS

Any questions, please contact the laboratory: Michelle 810-229-7575 ext. 29

APPENDIX C: Terms and Abbreviations

Absorbance - A measure of the decrease in incident light passing through a sample into the detector.

Absorption - To absorb. The process of incorporating a substance (liquid or gas) into the body of another substance (solid).

Accuracy - The nearness of a result or the mean (x) of a set of results to the true value. Accuracy is assessed by means of reference samples and percent recoveries.

Acid - An inorganic or organic compound that 1) reacts with metals to yield hydrogen; 2) reacts with a base to form salt; 3) dissociates in water to yield hydrogen ions; 4) has a pH of less than 7.0; and 5) neutralizes bases or alkalies. All acids contain hydrogen and turn litmus paper red. They are corrosive to human tissue and are to be handled with care.

Adsorb - To attract and retain gas, liquid, or dissolved substances on the surface of another material.

Adsorbtion - To adsorb. Adhesion of molecules of gas, liquid, or dissolved solids to a surface. Adsorbtion is a surface phenomenon.

Aliquot - A measured portion of a sample taken for analysis.

Ambient - Usual or surrounding conditions of temperatures, humidity, etc.

Analysis Date/Time - The date and time of the introduction of the sample, standard, or blank into the analytical system.

Analyte - The element or ion compound an analyst seeks to determine; the element of interest.

Analytical Batch - The basic unit for analytical quality control is the analytical batch. The anlytical batch is defined as samples which are analyzed together with the same method sequence manipulations common to each sample within the same time periods or in continuous sequential time periods. Samples in each batch should be of similar composition (e.g. groundwater, sludge, soil, etc.)

Analytical Sample - Any solution or media introduced into an instrument on which an analysis is performed excluding instrument calibration, initial calibration verification, initial calibration blank, continuing calibration verification and continuing calibration blank. Note the following are all defined as anlytical samples: undiluted and diluted samples, pre-digestion spike samples, duplicate samples, serial dilutions samples, analytical spike samples, post-digestion spike samples, interference check samples, laboratory control sample, preparation blank, and linear range analysis sample.

Analytical Spike - (Inorganic Analysis) The post-digestion spike. The addition of a known amount of standard after digestion.

Aromatics - A class of cyclic hydrocarbon compounds with the simplest member of the series being benzene. These unsaturated, multi-ringed compounds are found in petroleum products and in emissions produced by coal burning power plants, engines that burn gasoline and diesel fuel, and incinerators used for refuse disposal. Many aromatic hydrocarbons are carcinogenic.

ASTM - American Society of Testing and Materials. An organization that devises consensus standards for materials characterization and use.

Average Intensity - (Inorganic Analysis) The average of two different injections; multiplying sequential spectrophotometric measurements.

Background Correction -(Inorganic Analysis) A technique to compensate for variable background contribution to the instrument signal due to matrix absorptions/emissions in the determination of trace elements.

Background Level - In air pollution control, the concentration of air pollutants in a defined area during a fixed period of time prior to initiating or stopping a controlled emission. In toxic substances monitoring, the average presence in the environment, originally referring to naturally occurring phenomena.

Base - Substances that usually liberate OH^- anions when dissolved in water. Bases react with acids to form salts and water. Bases have a pH > 7, turn litmus paper blue, and may be corrosive to human tissue. A strong base is called alkaline or caustic. Examples are lye and DRANO.

Batch - A group of samples prepared at the same time in the same location using the same method.

Bias - Consistent deviation of measured values from the true value, caused by systematic errors in a procedure.

Biochemical Oxygen Demand (BOD) - A measure of the amount of oxygen consumed in the biological processes that break down organic matter in water. The greater the BOD, the greater degree of pollution.

Blank - An artificial sample designed to monitor the introduction of artifacts into the process. For aqueous samples, reagent water is used as a blank matrix; however, a universal blank matrix does not exist for solid samples, but sometimes clean sand is used as a blank matrix. The blank is taken through the appropriate steps of the process.

BNA - Base, Neutral, Acid Extractable Compound

Bromofluorobenzene (BFB) - Compound used to establish mass spectral instrument performance for volatile analyses. Also used as a surrogate for volatile organic analysis.

Buffer - A substance that reduces the change in hydrogen ion concentration (pH) otherwise produced by adding acids or bases to a solution. A pH stabilizer.

Calibration - (Inorganic Analysis) The establishment of an analytical curve based on the absorbance, emission intensity, or other measured characteristic of known standards. The calibration standards must be prepared using the same type of acid and reagents or concentration of acids as used in the sample preparation.

Calibration Blank - (Inorganic Analysis) An organic or aqueous solution that is as free of analytes as possible and prepared with the same volume of chemical reagents used in the preparation of the calibration standards and diluted to the appropriate volume with the same solvent (water or organic) used in the preparation of the calibration standard. The calibration blank is used to give the null reading for the instrument response versus concentration calibration curve. One calibration blank should be analyzed with each analytical batch or every method specified number of samples, whichever is greater.

Calibration Check - Verification of the ratio of instrument response to analyte amount, a calibration check is done by analyzing for analyte standards in an appropriate solvent. Calibration check solutions are made from a stock solutions that is different from the stock used to prepare standards.

Calibration Check Standard - Standard used to determine the state of calibration of an instrument between periodic re-calibrations.

Carcinogen - A cancer causing substance.

CAS Registration Number - Chemical Abstracts Service. An assigned number used to identify a chemical. CAS is an organization that indexes information published in the *Chemical Abstracts* by the American Chemical Society and that provides index guides by which information about particular substances may be located in the abstracts.

CCC - Calibration Check Compound.

CERCLA - The Comprehensive Environmental Response, Compensation, and Liability Act. The Superfund Law, Public Law PL 96-510, found at 40 CFR 300. The EPA has jurisdiction. Enacted Dec.11, 1980, and amended thereafter, CERCLA provides for identification and cleanup of hazardous materials released over the land and into air, waterways, and groundwater. It covers areas affected by newly released materials and older leaking or abandoned dump sites. CERCLA established the superfund, a trust fund to help pay for cleanup of hazardous materials sites. The EPA has authority to collect cleanup costs from those who release the waste material.

CFR - *Code of Federal Regulations*. A collection of the regulations established by law.

Check Sample - A blank which has been spiked with the analyte(s) from an independent source in order to monitor the execution of the analytical method is called a check sample. The level of the spike is usually at the regulatory action level when applicable. Otherwise, the spike shall be a t 5 times the estimate of the quantification limit.

Check Standard - A material of known composition that is analyzed concurrently with test samples to evaluate a measurement process. An analytical standard that is analyzed to verify the calibration of the analytical system. One check standard should be analyzed with each analytical batch or every 20 samples, whichever is greater.

Chemical Oxygen Demand (COD) - A measure of the oxygen required to oxidize all compounds in water, both organic and inorganic.

Chlorinated Hydrocarbons - A broad class of chemical compounds that contain chlorine as part of their molecular structure. Chlorinated pesticides such as DDT, aldrin, dieldrin, and mirex are examples. Other examples are chlorinated solvents such as chloroform, methylene chloride, methyl chloride, vinyl chloride, and 1,2,3-tichloropropane.

Coefficient of Variation (CV) - The standard deviation as a percent of the arithmetic mean.

Coliform - The coliform group consists of several genera of bacteria belonging to the family Enterobacteriaceae.

Confidence Coefficient - The probability, % that a measurement result will lie within the confidence interval or between the confidence limits.

Contaminant - Any physical, chemical, biological, or radiological substance that has an adverse affect on air, water, or soil.

Continuing Calibration - (Organic Analysis) Analytical standard run every 12 hours to verify the calibration of the GC/MS system.

Continuing Calibration - (Inorganic Analysis) Analytical standard run every 10 analytical samples to verify the calibration of the analytical system.

Control Limits - A range within which specified measurement results must fall to be compliant. Control limits may be mandatory, requiring corrective action if exceeded, or advisory, requiring that non-compliant data be flagged.

Corrective Action - Under the 1984 amendments to the RCRA, the EPA can require RCRA permittees or applicants for permits to take corrective action for releases of hazardous waste or hazardous constituents from solid waste management units (SWMUs) at a permitted facility.

Correlation Coefficient - A number (r) which indicates the degree of dependence between two variables (concentration – absorbance). The more dependent they are the closer the value to 1. Determined on the basis of the least squares line.

Corrosive - A chemical that causes visible destruction of or irreversible alterations in living tissue by chemical action at the site of contact, which causes a severe corrosion rate in steel or aluminum.

ft^3 - Cubic foot.

m^3 - Cubic meter.

CWA - Clean Water Act.

Decafluorotriphenylphosphine (DFTPP) - (Organic Analysis) Compound used to establish mass spectral instrument performance for semi-volatile analysis.

Degradation - The process by which a chemical is reduced to a less complex form.

Density - Ratio of weight (mass) to volume of a material, usually in grams per cubic centimeter or pounds per gallon.

Dissolved Metals - (Inorganic Analysis) Analyte elements which have not been digested prior to analysis and which will pass through a 0.45 µm filter.

Dissolved Oxygen (DO) - The oxygen freely available in water. Dissolved oxygen is vital to fish and other aquatic life and for the prevention of odors.

Dissolved Solids - Disintegrated organic and inorganic material contained in water. Quantitation of soluable ions and compounds. Excessive amounts make water unfit to drink or use in industrial processes.

Dry Weight - The weight of a sample based on percent solids. The weight after drying in an oven.

Duplicate - A second aliquot of sample that is treated the same as the original sample in order to determine the precision of a method.

Duplicate Samples - Duplicate samples are two separate samples taken from the same source (i.e., in separate containers and analyzed independently)

EDL - Estimated Detection Limit

Effluent - Treated or untreated wastewater that flows out of a treatment plant, sewer, or industrial outfall. Generally refers to wastes discharged into surface waters.

Environmental Sample - An environmental sample or field sample is a representative sample of any material (aqueous, non-aqueous, or multi-media) collected from any source for which determination of composition or contamination is requested or required. Samples are usually classified as drinking water, water/wastewater, sludge, or waste.

EPA - Environmental Protection Agency

Equipment Blank - An organic and aqueous solution that is as free of anlayte as possible and is transported to the site, opened in the field, and poured over or through the sample collection device, collected in a sample container, and returned to the laboratory for anlaysis.

EQL - Estimated Quantitation Limit

Extractable - (Organic Analysis) A compound that can be partitioned into an organic solvent from the sample matrix and is amenable to gas chromatography. Extractables include semi-volatile (BNA) and pesticide/Aroclor compounds.

EPTOX - Extraction Procedure Toxicity Test. A series of laboratory tests designed to determine the level of toxicity in solid waste or landfill materials.

Field Blank - An organic or aqueous solution that is as free of analyte as possible and is transferred from one vessel to another at the sampling site and preserved with the appropriate reagents. This serves as a check on reagent and environmental contamination. One field blank should be analyzed with each analytical batch or every 20 samples, whichever is more frequent.

FLAA - Flame Atomic Absorption. Atomic absorption which utilizes flame for atomic excitation.

Flash Point - Lowest temperature at which a flammable liquid gives off sufficient vapor to form an ignitable mixture with air near its surface within a vessel.

The *Federal Register* - A daily publication that lists and discusses Federal regulations.

GC/MS - Gas Chromatography/Mass Spectrometry.

GFAA - Graphite Furnace Atomic Absorption. Atomic absorption which utilizes a graphite cell for excitation.

Hazardous Waste - By-products of society that can pose a substantial or potential hazard to human health or the environment when improperly managed. Possesses at least one of four characteristics (ignitibility, corrosivity, reactivity, or toxicity) or appears on special EPA lists.

Holding Time - The elapsed time expressed days from the date of receipt of the sample by the Contractor until the date of its analysis.

Hydrocarbon - Any of a series of chemical compounds that consist entirely of carbon and hydrogen.

ICP/MS - Inductively Coupled Plasma/Mass Spectrometry.

ICS - Interference Check Standard.

ICP - Inductively Coupled Plasma. A technique for the simultaneous or sequential multi-element determination of elements in solution. Atomic absorption which utilizes Argon plasma for atomic excitation.

Initial Calibration - Analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the analytical detector or method.

Instrument Detection Limit (IDL) - Determined by multiplying by three the standard deviation obtained for the analysis of a standard solution (each analyte in reagent water) at a concentration of 3 to 5 times IDL on three nonconsecutive days with seven consecutive measurements per day.

Internal Standard - Compound(s) added to every standard, blank, matrix spike, matrix spike duplicate, sample (for VOAs), sample digestates (for ICP-MS) and sample extract (for semi-volatiles) at a known concentration, prior to analysis.

Laboratory Control Sample (LCS) - A control sample of known composition. Aqueous and solid laboratory control samples are analyzed using the same sample preparation, reagents, and analytical methods employed for the EPA samples received.

Laboratory Control Standard - A standard, usually certified by an outside agency, used to measure the bias in a procedure.

Laboratory Fortified Blank (LFB) - An aliquot of laboratory reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like the sample and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

Limit of Quantitation (LOQ) - The constituent concentration that produces a signal sufficiently greater than the blank that it can be detected with the specified limits by good laboratories during routine operating conditions.

Linear Range, Linear Dynamic Range - (Inorganic Analysis) The concentration range over which the analytical response remains linear with concentration.

Lower Limit of Detection (LLD) - The constituent concentration in reagent water that produces a signal above the mean of blank analyses. This sets both Type I and Type II errors at 5%. Other names for this limit are detection limit and limit of detection.

Matrix - The material of which the sample to be analyzed is composed.

Matrix Modifier - (Inorganic Analysis) Reagents used in AA to lessen the effects of chemical interferents, viscosity, and surface tension.

Matrix Spike (MS) - Aliquot of sample spiked with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

Matrix Spike Duplicate (MSD) - A second aliquot of the same matrix as the matrix spike that is spiked in order to determine the precision of the method.

Maximum Contaminant Levels (MCLs) - The maximum level of contamination allowed in any surface or ground water under the Safe Drinking Water Act for certain identified pollutants. The maximum permissible level of a contaminant in water delivered to any user of a public water system. MCLs are enforceable standards.

MDL - Method Detection Limit. The constituent concentration that, when processed through the complete method, produces a signal with a 99% probability that it is different from the blank. For seven replicates of the sample, the mean must be 3.14 above the blank where o is the standard deviation of the seven replicates.

Method Blank - An analytical control consisting of all reagents, internal standards and surrogate standards, that is carried through the entire analytical procedure. The method blank is used to define the level of laboratory background and reagent contamination.

Method of Standard Additions - (Inorganic Analysis) The addition of 3 increments of a standard solution (spikes) to sample aliquots of the same size. Measurements are made on the original and after each addition. The slope, x-intercept and y-intercept are determined by least-square analysis. The analyte concentration is determined by the absolute value of the x-intercept. Ideally, the spike volume is low relative to the sample volume (approximately 10% of the volume). Standard addition may counteract matrix effects; it will not counteract matrix effects; it will not couteract spectral effects. Also referred to as Standard Addition.

MQL - The method quantification limit (MQL) is the minimum concentration of a substance that can be measured and reported.

MSDS - Material safety data sheet. OSHA has established guidelines for the descriptive data that should be concisely provided on a data sheet to serve as the basis for written hazard communication programs. The thrust of the law is to have those who make, distribute, and use hazardous materials responsible for effective communication.

NA - Not applicable, not available.

PCBs - A group of toxic, persistent chemicals (polychlorinated biphenyls) used in transformers and capacitors for insulating purposes and in gas pipeline systems as lubricant. Further sale banned by law in 1979.

Percent Moisture - An approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at 105°C. The percent moisture determined in this manner also includes contributions from all compounds that may volatilize at or below 105°C, including water.

Percent Solids - The proportion of solid in a soil sample determined by drying an aliquot of the sample.

Performance Evaluation (PE) Sample - A sample of known composition provided by EPA for contractor analysis. Used by EPA to evaluate contractor performance.

Pesticide - Substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest. Any substance or mixture of substances intended for use as a plant regulator, defoliant, or desiccant.

pH - "Hydrogen ion exponent" A measure of hydrogen ion concentration. A scale (0-14) representing an aqueous solution's acidity or alkalinity. Low pH values indicate acidity and high values, alkalinity. The scale's mid-point, 7, is neutral.

ppb - Parts per billion.

ppm - Parts per million.

PQL - The practical quantitation limit is the lowest level that can be reliable achieved within the specified limits of precision and accuracy during routine laboratory operating conditions.

Precision - Precision is the agreement between a set of replicate measurements without assumption of knowledge of the true value.

Quality Assurance - A definitive plan for laboratory operation that specifies the measures used to produce data of known precision and bias.

Quality Control - Set of measures within a sample analysis methodology to assure that the process is in control.

Reagent Blank - A solution that is as free of analytes as possible and contains all the reagents in the same volume as used in the processing of the samples. One reagent blank should be prepared for every analytical batch or for every 20 samples, whichever is greater.

Reagent Grade - Analytical reagent grade, ACS reagent grade and reagent grade are synonymous terms for reagent which conform to the current specification of the Committee on Analytical Reagents of the American Chemical Society.

Reagent Water - Water in which an interferent is not observed at or above the minimum quantitation limit of the parameters of interest.

Relative Percent Difference (RPD) - To compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero.

Relative Response Factor (RRF) - A measure of the relative mass spectral response of an analyte compared to its internal standard.

Replicate - Repeated operation occurring within an analytical procedure. Two or more analyses for the same constituent in an extract of a single sample constitutes replicate extract analyses.

Replicate Sample - A replicate sample is a sample prepared by dividing a sample into two or more separate aliquots. Duplicate samples are considered to be two replicates.

Retention Time Window - Usually defined as three times the standard deviation of the absolute of relative RT of an analyte standard injected over the course of a 72- hour period.

Semi-volatile Compounds - (Organic Analysis) Compounds amenable to analysis by extraction of the sample with an organic solvent. Used synonymously with Base/Neutral/Acid (BNA) compounds.

Serial Dilution - The dilution of a sample by a factor of five. When corrected by the dilution factor, the diluted sample must agree with the original undiluted sample within specified limits. Serial dilution may reflect the influence of interferents.

SIM - Selected Ion Monitoring

Sludge - A semisolid residue from any of a number of air or water treatment processes. Sludge can be a hazardous waste.

SOP - Standard Operating Procedure.

SOW - Statement of Work.

SPCC - System Performance Check Compound.

Stock Solution - Standard solution which can be diluted to derive other standards.

Surrogate - Surrogates are organic compounds which are similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in environmental samples. Percent recoveries are calculated for each surrogate.

Suspended Solids - Small particles of solid pollutants that float on the surface of, or are suspended in, sewage or other liquid.

Tentatively Identified Compounds (TIC) - Compounds detected in samples that are not target compounds, internal standards, system monitoring compounds, or surrogates.

Total Metals - (Inorganic Analysis) Analyte elements which have been digested prior to analysis. Measurement of acid soluable metal in a sample.

Total Suspended Solids (TSS)- A measure of the suspended solids in wastewater, effluent, or water bodies.

Toxicity Characteristic Leaching Procedure (TCLP) - Analytical method used to determine the mobility of organic and inorganic contaminants present in liquid, solid, and multiphase wastes. If an extract from a representative sample is shown to contain any contaminant in an amount exceeding levels allowed regulation, the waste is banned for land disposal unless properly treated.

Trip Blank - Usually an organic or aqueous solution that is as free of analyte as possible and is transported to the sampling site and returned to the laboratory without being opened. This serves as a check on sample contamination origination from sample transport, shipping, and from the site conditions. One trip blank should be analyzed with each analytical batch or every 20 samples, whichever is greater.

Tuning Solution - A solution which is used to determine acceptable instrument performance prior to calibration and sample analyses.

Turbidity - Haziness in air caused by the presence of particles and pollutants. A similar cloudy condition in water caused by suspended silt or organic matter.

Type I Error - Also called alpha error, is the probability of deciding a constituent is present when it actually is absent.
Type II Error - Also called a beta error, is the probability of not detecting a constituent when it is actually present.
Volatile - Description of any substance that evaporates easily.
Volatile Compounds - (Organic Analysis) Compounds amenable to analysis by the purge and trap technique. Used synonymously with purgeable compounds.
Wet Weight - The weight of a sample aliquot including moisture (undried).

APPENDIX D: SAMPLE ACCEPTANCE POLICY

Below are the terms and conditions required by Brighton Analytical, LLC for the acceptance/rejection of samples.

SAMPLE SUBMISSION:

1. All samples must be accompanied by a complete chain-of-custody which will include sample identification, location, date and time of collection, collector's name, preservation type/bottle type, sample matrix, and any remarks concerning the sample, i.e. contains radioactive materials or hazardous. The chain-of-custody form authorizes Brighton Analytical to perform the testing it summarizes.
2. Attach a quote, if applicable, to the chain of custody to ensure accurate invoicing.
3. All samples must be properly labeled by the customer and in appropriate sample container/volumes.
4. If samples not within hold time, the client is informed and this is noted on the Chain of Custody and final report if analysis proceeds.
5. New clients are required to pay all fees up front before analytical testing begins. After that, clients are to submit a credit application and all work will be billed upon completion of the analytical testing.
6. Any criteria not met will be clearly flagged on the chain of custody and final report.

LABORATORY PROCEDURE:

1. All samples are properly labeled by the laboratory to include unique identification with a water resistant label and indelible ink.
2. If samples show signs of damage or contamination, notify the client by fax and/or phone immediately. Place samples on hold until the client advises the lab to proceed or cancel the project. If samples are inadequately preserved, preserve the samples in correct preservative/containers and clearly note on the Chain of Custody.
3. Brighton Analytical performs the testing requested on the Chain of Custody. If changes occur that are different than the requested tests, it must be submitted in writing via fax or other. If original sample analysis is cancelled, changed, or put on hold, any analysis that has already been performed/completed before the change, the client may be responsible for additional fees.
4. Brighton Analytical will dispose of the clients samples 60 days after receipt unless the client requests the samples to be held an additional amount of time, up to 6 months total, or return of the samples. Samples that are hazardous, such as PCBs, may be returned to the client for disposal.
5. If samples have to be prepped or analyzed "Rush" due to holding time issues, the client is responsible for additional fees. Brighton Analytical will confirm this with the client prior to prepping/analyzing.
6. Brighton Analytical accepts no legal responsibility for the purpose for which the test results are applied and/or interpretations/conclusions based on the test results.

FINAL REPORTS AND INVOICING:

1. Analytical reports are provided to the client no more than 10 business days from receipt. Data is retained for a minimum of 5 years.
2. Results of sample analysis only relate to samples submitted for the tests requested.
3. Reports should not be reproduced except in full unless otherwise authorized by the lab.
4. Additional copies of reports are provided for a $20 fee.
5. The client is responsible for cost of shipment or delivery of samples to the laboratory unless prior arrangements have been made for sample pickup by Brighton Analytical which is found in the quote.
6. Payment for analytical services and all fees are to be made within 30 days. The client is responsible for payment to Brighton Analytical and it is not contingent on third party payments.

LIABILITIES:

1. Brighton Analytical will indemnify and hold the client harmless from and against demands, damages, and expenses caused by our negligent acts and omissions and breach of contract, and by the negligent acts and omissions and breach of contract of the persons for whom we are legally responsible. The client agrees to indemnify and hold Brighton Analytical harmless from and against demands, damages, and expenses caused by the clients negligent acts and omissions and breach of contract and by the negligent acts and omissions and breach of contract of persons for whom the client is legally responsible.
2. Brighton Analytical's total liability to you, the client, for any and all injuries, claims, losses, expenses, damages, or claim expenses arising under these Terms and Conditions from any cause(s), shall not exceed $1,000,000. Such causes include, but not limited to, Brighton Anaytical's negligence, errors, omissions, strict liability, breach of contract or breach of warranty.
3. In the event of a dispute arising under these terms and conditions, Brighton Anaytical shall resolve the dispute by good faith negotiations between the parties involved. If good faith negotiations fail, any dispute shall be submitted to non-binding mediation, except to the extent necessary to obtain injunctive relief. Each party is responsible for their own mediation fees.
4. Except for the obligation to pay for services rendered, neither party herto shall be liable for its failure to perform hereunder in whole or in part due to contingencies beyond its reasonable control. These contingencies include but are not limited to fire, acts of God, equipment failure, matrix interference, injunction to compliance with any law, regulations or order of any governmental body or any instrumentality thereof whether now existing or hereafter created.
5. Neither party will be liable to the other for special incidental, consequential, or punitive losses or damage including, but not limited to, those arising from delay, loss of use, loss of profits or revenue or the cost of capital.